

CHEMISTRY FOR CHANGING TIMES

John W. Hill

Surjeet Publications

✓
Third Edition

Chemistry for Changing Times

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Preface

TO THE STUDENT

Welcome to Our Chemical World

Chemistry is fun. Through this book, I would like to share with you some of the excitement of chemistry and some of the joy in learning about it. I hope to convince you that chemistry does not need to be excluded from your learning experiences. Learning chemistry will enrich your life—now and long after this course is over—through a better understanding of the natural world, the technological questions now confronting us, and the choices we must face as citizens within a scientific and technological society.

Chemistry Directly Affects Our Lives

How do our bodies work? How can foods make us fat? What happens to our bodies when we go on a low-carbohydrate diet? Why do our moods change from happy to sad? What do drugs do to our bodies? How does penicillin kill bacteria without harming our healthy body cells? Chemists have found answers to questions like these and continue to seek the knowledge that will unlock still other secrets of our universe. As these mysteries are resolved, the direction of our lives often changes—sometimes dramatically. Your knowledge of chemistry will help you to make appropriate decisions in the future.

Chemistry Is Life

Our bodies are intricate chemical factories. They are durable but delicate systems. A myriad of chemical reactions are constantly taking place within us which allow our bodies to function properly. Thinking, learning, feeling happy or sad, putting on too much weight or not gaining enough, and virtually all life processes are made possible by these chemical reactions. Everything that we ingest is part of a complex process that determines whether our bodies work effectively or not. The

consumption of some substances can initiate chemical reactions that will stop body functions altogether. Other substances, if consumed, can cause permanent handicaps, and others can make living less comfortable. A proper balance of the right foods provides the chemicals and generates the reactions we need in order to function at our best. The knowledge of chemistry that you will soon be gaining will help you to better understand how your body works so that you will be able to take proper care of it.

Chemistry and Your Future

By choosing this course, you have indicated that you are not planning a career in chemistry. Should you change your mind, there are other books and other courses. Even if this turns out to be your last chemistry course, you are not "finished" with chemistry. We live in a chemical world—a world of nuclear wastes, dwindling petroleum reserves, drugs, biocides, food additives, fertilizers, detergents, plastics and pollutants. Knowledge of chemistry will help you to better understand the benefits and hazards of this world and enable you to make intelligent decisions in the future.

Changing Times

We live in a world of increasingly rapid change. It has been said that the only constant is change itself. At present, we are facing some of the greatest problems that humans have ever encountered, and the dilemmas with which we are now confronted seem to have no perfect solutions. We are sometimes forced to make a best choice among only bad alternatives, and our decisions often provide only temporary solutions to our problems. Nevertheless, if we are to choose properly, we must understand what our choices are. Mistakes can be costly and they cannot always be rectified. We can best avoid mistakes by collecting as much information as possible before making critical decisions. Science is a means of gathering and evaluating information, and chemistry is central to all the sciences.

After Completing the Course

Student interest continues long after conclusion of my course. It is most gratifying to see students, who arrived in my course with fear and uncertainty and a definite bias against chemistry, leave the course with a new-found curiosity about chemistry and its impact on their lives. After completing my course, many students have joined environmental action groups, collected samples for monitoring air and water quality, and formed a "hot line" telephone service to help students with drug problems.

Major Changes in This Revision

The entire book has been updated. The last edition's chapter on energy has been expanded into two separate chapters, as have the chapters on food additives and organic chemistry. New chapters have been added that deal with the following topics: names, formulas, and equations; acids and bases; oxidation and reduction; and cosmetics. Chapters one and two from the second edition have been condensed and combined into one, and some of the anecdotes have been discarded. More information has been presented via figures and tables, and more efficient use has been made of the margins. Virtually no portion of the previous edition has been left unchanged, but this revision still retains the spirit of that work.

chemistry is not always easy, but it can be rewarding if the information is conveyed in a clear and understandable way. With this thought in mind, we have tried to create a chemistry textbook that is both clearly readable and thoroughly enjoyable—and we believe we have succeeded in doing so.

Units of Measurement

The metric system has been adopted by most of the world, and the modern version, the International System of Units (SI), is used in many countries, especially by scientists. What units of measurement should be used in a chemistry text designed for use by students of the humanities and the social sciences? We feel that students will encounter both the old metric system and the new SI version, in addition to the English system, in their everyday lives. Therefore, we have used the units that they are most likely to encounter—Calories, not joules, when discussing weight loss or gain, for example. Nevertheless, we have used SI units in the presentation of most chemical principles, and we have used the SI spellings (litre, not liter) and symbols (K, not °K) where they do not present a barrier to learning.

Complicated Chemical Structures

Structures of complicated molecules are presented in the text, particularly toward the end, but students should not feel that they are expected to memorize them. They have been presented merely to emphasize the fact that these structures are known and that molecular properties depend upon them. Students may, however, come to recognize familiar functional groups, even with respect to the most complicated molecules.

TO THE INSTRUCTOR

The Revision

The previous editions of *Chemistry for Changing Times* were written with the firm conviction that chemistry can be presented in an intellectually honest way to students who have little background and no prior interest in chemistry. That assumption also underlies this revision, as does the belief that a course for students not majoring in science must be taught differently than a course taught to science majors.

Our Goals

We can no longer feel we have done our duty to nonscience students and to society by teaching only traditional chemistry courses. A traditional course will not stimulate a typical nonscience student's interest or kindle much of a desire to know more about the world. Most of the world's problems won't be solved without intelligent applications of chemistry, and if we fail to motivate our students or if we allow them to complete our courses without having gained an understanding of or an appreciation for the chemical world, all of society loses. We are living in an age where difficult daily decisions that affect our health and the future of the world prevail, and the stakes are enormously high. If we fail to take advantage of our present opportunities, we will be contributing to the very maladies we hope to correct.

Our Students

Generally, students enrolled in this course are not interested in the austere abstractness and the elegant mathematics of the physical theories that we scientists find so beautiful. If they were, they would most likely be science majors. Because of

their temperament and training these students are not prepared to understand the awesome mathematical theories of quantum mechanics and thermodynamics. Even the simplest stoichiometric relationships inspire fear in many of these students. The essential quantitative nature of chemistry must be presented to students with care to avoid intimidation.

Our Objectives

The principal objectives in a chemistry course for nonscience students are these:

- Design your chemistry course to attract as many students as possible. If they don't enroll, you won't have the opportunity to teach them.
- Have students study examples of current topics in chemistry so that they will incorporate into their lives a sense for how chemists approach and solve problems.
- Induce students to relate chemical problems to their own lives so that they will be better able to appreciate the significance of such problems.
- Instill in students an appreciation for chemistry as an open-ended learning experience that will continue throughout their lives. Chemistry should not be a subject that is memorized before the final exam and then quickly forgotten.
- Acquaint students with the scientific method so that they will be able to distinguish between science and technology.

These objectives have been met to a most gratifying extent in my own course. Course enrollment rose sharply during the early years of the course, and it has continued to rise more rapidly than overall university enrollment.

Problems

In response to surveys conducted by the publisher, previous users of this book have expressed a desire for more study problems. Consequently, I have added problems to each chapter. Instructors should assign the problems at their own discretion. You should present problems and exercises of your own if you want students to develop skills in special areas. Answers to selected problems are given in the appendix. Detailed, worked-out answers to all of the problems are given in the study guide.

References and Suggested Readings

At the end of each chapter, you will find a list of recommended books and articles. Students whose interest and enthusiasm have been sparked can delve more deeply into those subjects about which they are curious. Instructors will also find this information helpful.

The Study Guide

A study guide is available for this edition to help students learn the material more effectively. For each chapter of the text, this guide provides an overview, a list of objectives, and a series of short-answer questions. The guide also provides additional problems as well as worked-out sample problems where appropriate. Use your own judgment to make additions to and deletions from the lists of objectives. (Actually, I'd be most pleased if you would share your suggestions for additions or

deletions with me.) The study guide contains worked-out solutions to all of the problems presented in the text.

The Instructor's Guide

An instructor's guide has also been prepared in conjunction with the text. This guide suggests course outlines for courses ranging in length from one quarter to one full year. The flexibility of these outlines will enable you to choose the material that best suits the particular needs of your students. The guide also lists sources of other printed educational material as well as audiovisual aids. Furthermore, it suggests lecture demonstrations and examination questions for each of the text's chapters. Teaching strategies for presenting difficult material are also provided. Many of the suggestions that have come from you, the users of *Chemistry for Changing Times*, have been incorporated in this guide, and additional suggestions are welcome anytime.

The Laboratory Manual

The laboratory manual, *Chemical Investigations for Changing Times*, is also available in a new, third edition. You will find shorter, cheaper, and safer experiments in this revised manual. You will discover that this greater number of experiments enables you to select experiments that are best suited to your style of teaching.

ACKNOWLEDGMENTS

I wish to thank everyone who has contributed suggestions in the preparation of this work. A special note of gratitude is due C.A. VanderWerf, University of Florida, for his many helpful suggestions, and for his kindness and thoughtfulness throughout our endeavors. Many thanks to my colleague Emerson Garver for his help and encouragement, given freely so many times, and to Peter Muto, who has served so long in the trenches, with hardly a quarter off for rest and relaxation. To Mike Keenan and Larry Scott, my thanks for advice on biochemistry and food chemistry.

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To all the others, please be assured that your suggestions were carefully considered. Many were incorporated, but obviously all could not be and keep within our goal of size and cost.

To Ina, my wife, and to our children, Cindy and Don, my gratitude for your patience during the many lonely evenings and weekends that this endeavor has cost our family. May I someday be able to repay you. And to Cindy, a special thanks for working with permissions and for providing ideas for several of the figures.

Above all, though, I would like to thank the many students who with zest and enthusiasm have gone on to learn for themselves more about chemistry than I ever taught them. Teaching is a joy, but learning is a real celebration. I have learned far more from my students than I can ever teach them; for that I am eternally grateful. Comments, corrections, suggestions, and criticisms are always welcome.

River Falls, Wisconsin

John W. Hill

January 1979

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chapter 1

Chemistry: A Science for All Seasons

Chemistry on the evening news—they call it a materials shortage. Chemistry in the newspapers—they call it an energy crisis.

You didn't know that was chemistry? Consider the usual definition: *chemistry* is a study of matter and the changes it undergoes. What is *matter*? It is the stuff of which all material things are made. We change matter to make it more useful. Most changes in matter are accompanied by changes in energy. Some matter we change to extract a part of its energy; for example, we burn gasoline to get energy to propel our automobiles.

More about matter and energy later. Indeed, matter and energy are what this book—and all of chemistry—is about. But chemistry isn't just something you hear or read about. You are a chemist. You practice chemistry every day.

You practice chemistry in the kitchen when you cook. You practice chemistry when you clean your house, wash your car, or paint a fence. You practice chemistry in the bathroom when you bathe and apply cosmetics. You practice chemistry when you take medicine or treat an injury. Indeed, some remarkable chemistry occurs while you eat or breathe and even while you sleep. Your body is the most miraculous of all the chemical factories on Earth. It takes the food you eat and turns it into muscle and blood and skin and bones and brains and a myriad of other marvelous things. Your body takes oxygen from the air and combines it with part of the food you eat to provide you with energy for every activity you undertake.

What is chemistry? It is a science that touches your life every moment. It deals with matter from the tiniest parts of atoms to the minutest materials of the complex human body. It goes beyond the individual to affect society as a whole, and it shapes our civilization.

Science and Technology: The Roots of Knowledge

Chemistry is a *science*, but what is a science? Let's examine the roots of science. Our study of the material universe has two facets: the *technological*, or *factual*, and the *philosophical*, or *theoretical*.

Technology arose long before science, having its origins in antiquity. The ancients used fire to bring about chemical changes. For example, they cooked food,

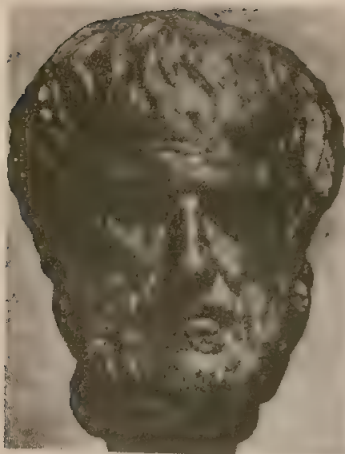


Figure 1.1 Aristotle (384-322 B.C.), Greek philosopher and tutor of Alexander the Great, believed that we could understand nature through logic. The idea of experimental science did not triumph over Aristotelian logic until about A.D. 1500. (Courtesy of the Smithsonian Institution, Washington, D.C.)

baked pottery, and smelted ores to produce metals such as copper. They made beer and wine by fermentation and obtained dyes and drugs from plant materials. These things—and many others—were accomplished without an understanding of the scientific principles involved.

The Greek philosophers were perhaps the first to formulate theories that explained the behavior of matter. However, the Greeks generally did not test their theories by experimentation. In spite of this shortcoming, the Greeks' view of nature, attributed mainly to Aristotle, was quite consistent internally, and it completely dominated natural philosophy for 2000 years.

Technology developed rapidly even during the Dark Ages (circa A.D. 500 to 1500) in Europe, in spite of the generally nonproductive Aristotelian philosophy that prevailed. The beginnings of modern science are more recent, however. What we now call science grew out of natural philosophy, that is, out of philosophical speculations about nature. By the seventeenth century, a changing attitude characterized by a reliance on experimentation had been developed by astronomers, physicists, and physiologists. With the emergence of the experimental method came the true beginnings of what we now call science.

The Baconian Dream

It was a philosopher, Sir Francis Bacon (1561-1626), who first had dreams about how science could enrich human life with new inventions and increased prosperity. By the middle of the twentieth century, it appeared that science and its application in technology had made the Baconian dream come true. Many dread diseases—smallpox, polio, plague—had been virtually eliminated. Fertilizers, pesticides, and scientific animal breeding had increased and enriched our food supply. Transportation was swift, and communication nearly instantaneous. New power sources had been discovered. Nuclear energy seemed to promise an unlimited quantity of power for our every need. New materials—plastics, fibers, metals, ceramics—were developed to improve our clothing and shelter.

Much of the twentieth century's technology has grown out of scientific discoveries, and new technological developments are used by scientists as tools for making new discoveries. These developments in science and technology are, to a considerable extent, the base of what we mean by the "modern" world.

The Carsonian Nightmare

The Baconian dream has lost much of its lustre during the last two decades. People learned that the products of science were not an unmitigated good. Some people began to predict that science might bring not wealth and happiness but death and destruction. Perhaps most noteworthy among these critics of modern technology was Rachel Carson, a biologist who had written several popular science books. In 1962, her poetic and polemic book *Silent Spring* was published. The book's main theme was that, through our use of chemicals to control insects, we are threatening the destruction of all life, including ourselves.

Spokespeople for the pesticide industry and their allies roundly denounced Carson as a "propagandist," while other scientists rallied to her support. The scientific community was divided into hostile camps. By the late 1960s, though, we had experienced massive fish kills, the threatened extinction of several species of birds, and the disappearance of fish from rivers, lakes, and areas of the ocean that had long been productive. The majority of scientists had moved into Carson's camp. Most of the remainder had moderated their criticism or become silent. Popular support for Carson's views was overwhelming.

Carson was not the first prophet of doom. As early as 1798, Thomas Malthus, in



Figure 1.2 Sir Francis Bacon (1561-1626), English philosopher and Lord Chancellor to James I. (Courtesy of the Smithsonian Institution, Washington, D.C.)

his "Essay upon the Principles of Population," had predicted that an increase in population more rapid than that of the food supply would lead to great famine. During the nineteenth century and for more than half of the twentieth, it appeared that science and technology had made a fool of Malthus. Food was abundant, at least in the developed countries. Scientific discoveries and technological developments enabled us to increase food production as rapidly as the population grew.

The 1970s brought further changes. Population growth threatened to outpace even the most optimistic projections of food production. Petroleum shortages caused what we have come to know as the energy crisis. Materials shortages became commonplace. Some scientists and others outside the scientific community projected a dismal future, while others confidently predicted that science and technology, properly applied, could save us from disaster.

What Science Is: A Journey, Not a Destination

What is science that scientists are able to dispute what is and what will be? Is science merely a guessing game in which one guess is as good as another? Unfortunately, textbooks often define science as a "body of knowledge." Often it is taught as a finished work rather than an ever-changing way of learning.

Science is not totally different from other disciplines. For example, creativity is central to science as well as to the arts and the humanities. And science is not always coldly logical to the exclusion of other human characteristics. Even Albert Einstein, perhaps the greatest scientist of this century, recognized that there was no logical path to some of the laws that he formulated. Even he relied on intuition—an intuition, however, based on experience and understanding.

What are some of the distinguishing characteristics of science? Science, like other disciplines, is organized into *concepts*. For example, we often speak of atoms as if they were readily observed, but the atomic concept is merely a convenience that helps to explain many observable properties of matter. It is not the body of facts that characterizes science but the organization given to facts. To be useful, concepts must have *predictive value*. If the atomic concept is to be useful, a scientist should be able to use it to predict how matter will behave.

Central to science are its processes, or methods. Scientists must make careful observations and accurate, quantitative measurements. Scientists record facts based upon their observations, but this is only a bare (but necessary) beginning to the intellectual processes. It is necessary to make careful observations, but it is essential that scientists be able to grasp the implications of their measurements. Scientists must recognize the variables in an experiment and be able to note the effect of changing one variable at a time. They must be able to pick out useful information and ignore irrelevancies.

Perhaps most basic to the methods of science is the ability to make *hypotheses* (guesses) that can be tested. This is the characteristic that serves most to distinguish science from the arts and the humanities. We can learn from individual experience, and we can learn about historical events, but the knowledge gained through science is different: it depends upon public phenomena that can be verified through repeated testing. Even educated guesses are of little value to scientists unless they can devise experiments to test their guesses. You may experience elation over a good grade in chemistry, but that experience is uniquely yours; others might not be at all elated with the same grade. But no matter who does the measuring, the boiling point of water and the speed of light remain the same. Scientific *facts* are verified by repeated testing.

Scientists often use *models* to help explain complicated phenomena. The word *model* has a somewhat different meaning in science than it does in everyday life. A

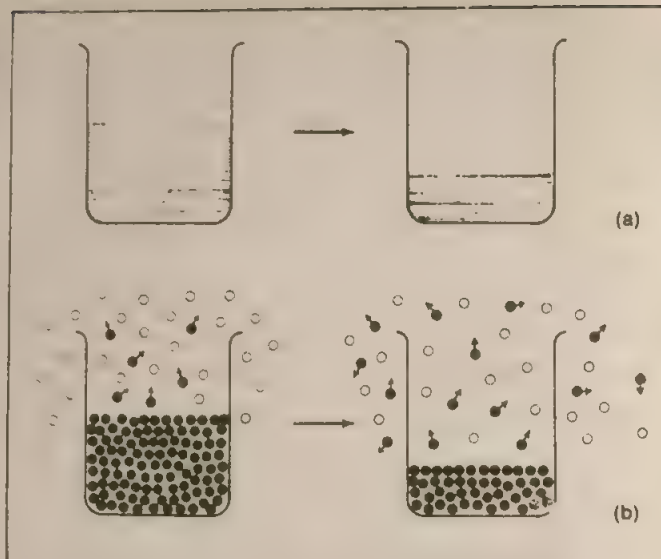


Figure 1.3 Rachel Carson at Woods Hole, Massachusetts, in 1951. (Edwin Gray Studio, copyright © 1951.)

Figure 1.4 The evaporation of water. (a) When a container of water is left standing open to the air, the water slowly disappears. (b) Scientists explain evaporation in terms of the motion of molecules.

● = water molecule

○ = air (nitrogen or oxygen) molecule



scientific model can be used to visualize the invisible. For example, when a glass of water is allowed to stand for a period of time, the water apparently disappears. The process is called evaporation. Scientists explain the phenomenon by means of the kinetic-molecular *theory*. According to the kinetic-molecular model, the liquid is made up of small, invisible particles called molecules. These molecules are in constant motion. In the bulk of the liquid, they are held together by forces of attraction. Some molecules near the surface of the liquid gain sufficient energy (through collisions with other molecules) to break the attraction of their neighbors

Let's summarize some of the differences between science and technology. These are not meant to be exact definitions or all-encompassing ones. These differences need not be memorized, but it might be helpful if you would keep them in mind—or refer back to this section—as you study subsequent chapters.

Technology is the sum total of the processes by which humans modify the materials of nature to better satisfy their needs and wants. These processes need not be based on scientific principles. For example, ancient peoples were able to smelt ores to produce metals, such as copper and iron, without having any understanding of the chemistry involved.

Science, on the other hand, is a way of trying to cope with our environment through an understanding of the nature of things. Scientific knowledge is organized into concepts that, when useful, have predictive value. Science is the theoretical framework that gives meaning to our factual knowledge. However, it is a constantly changing framework, for scientific models are constantly being reevaluated and revised as new data are obtained. An artist might experiment with clay to produce new art forms. A scientist, knowing the structure and composition of clay, might modify it to produce a new material. This modification would be based on an understanding of the arrangements of the atoms in the clay. The scientist probably would use models to *predict* how certain changes would affect the properties of the clay. The artist, most likely, would simply change the formulation and see what happened.

and escape from the liquid. These molecules are dispersed among the widely spaced air molecules; thus, the water disappears. For the scientist, it is much more satisfying to understand evaporation than merely to have a name for the process.

Successful scientists can deduce evidence from a model. Truly outstanding scientists may invent their own models (as have James Watson and Francis Crick, whose work is discussed in chapter 11).

There is no single scientific method that, when followed, produces guaranteed results. Scientists observe, gather facts, and make hypotheses, but somewhere along the way they must test their hunches and their organization of facts by experimentation. Scientists, like other human beings, use their intuition and form generalities from a few known facts. Sometimes they are wrong. Results of scientific experiments are published in scientific journals. These results are read—and often checked—by other scientists in all parts of the world. To become an acceptable part of the body of knowledge, the results must be reproducible.

Scientists also extend each other's work, sometimes creating a bandwagon effect. One breakthrough may result in the unleashing of vast quantities of new data and in the development of new concepts. For example, it was long thought that "inert gases" such as xenon formed no compounds. In 1962, Neil Bartlett (then at the University of British Columbia and now professor of chemistry at the University of California, Berkeley) managed to form a compound of xenon. Soon research chemists all over the world were synthesizing compounds of xenon and of other so-called inert gases. These experiments also led to significant changes in the theory of chemical bonding.

Thus, contrary to an often expressed popular notion, scientific knowledge is not absolute. Science is cumulative, but the body of knowledge is active and never final. New facts and new concepts are always being added. Old concepts or even old "facts" are discarded as new tools, new questions, and new techniques reveal new data and generate new concepts. To understand what science is, we have to observe what the whole worldwide community of scientists has done over several years; we cannot just look over the shoulder of a single scientist for a few days.

Science Copes

Science is a way of trying to cope with our environment, although it is not the only way. In primitive societies, magic is a common method of trying to cope. The primitive notes that thunder often precedes rain and concludes that beating drums, shouting, and making other thunderlike noises should cause rain to fall. A scientist, by carefully collecting and contemplating data, could easily show that this is a mistaken assumption of cause and effect. For most of the twentieth century, most educated people placed their faith in science as a way of understanding nature. In recent years, however, the resurgence of astrology and other mystic traditions has indicated the public's lack of confidence in the ability of science to cope with environmental problems.

Primitive religions were another way of trying to cope with the environment. It was assumed that the environment was controlled by supernatural powers and that establishing a favorable relationship with these controlling powers might bring about the desired result. For example, to cause rain to fall, a person might have sacrificed a precious object to the deity that governs weather.

Science, as a way of coping with the environment, involves the experimental establishment of cause and effect. For example, scientists have learned that water vapor condenses on small dust particles, called nuclei, to form raindrops. Therefore, scientists try to induce rainfall by seeding clouds with artificial nuclei. That such seeding is only somewhat successful in producing rain and that it raises innumerable

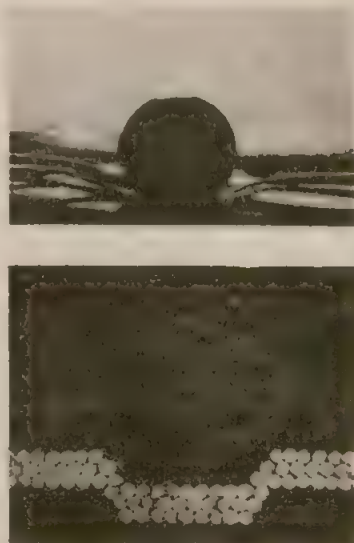


Figure 1.5. Another example of how a scientist uses models. (a) A steel ball striking the surface of a silicone liquid. (b) How a scientist might visualize the process in terms of an atomic model. (From the film *Wondering about Things*. Courtesy of Dow Corning Corporation, Midland, Mich.)

economic, political, and ethical questions also serve to point out some of the limitations of science.

What Science Cannot Do

We sometimes hear scientists and nonscientists alike state that we could solve all our problems if we would only use the scientific method in attacking them. We have seen already that there is no single scientific method. But why can't the procedures of the scientist be applied to social, political, ethical, and economic problems? Why do scientists disagree when they try to predict the future?

The answer usually lies in the ability to control variables. If, for example, we wanted to study in the laboratory how the volume of gases varies with changes in pressure, we would hold such factors as temperature and the amount and kind of matter constant. If, on the other hand, an economist wished to determine the effect of increased interest rates on the rate of unemployment, he or she would find it difficult, if not impossible, to control such variables as the level of governmental expenditures, the rate of business expansion, the needs of the armed forces, the number of high school and college graduates (and dropouts) entering the job market, and so on. Imagine, then, the difficulties encountered by a sociologist trying to predict the effect of a technological innovation, such as a communications satellite, upon whole populations.

We cannot control variables in social "experiments" (for example, public school desegregation) as we can in laboratory experiments. Therefore, a scientist would not be in any better position than any other citizen to decide whether desegregation is good or evil.

Figure 1.6 is a rough graph showing how the number of variables increases as we go from an exact science such as physics to the very complex social sciences. Notice that there is overlap between disciplines. The boundaries in the graph are crude approximations at best. A more accurate representation (but one much harder to draw) would show overlap between *all* the disciplines—even between physics and the social sciences.

Social scientists have become more productive by using some of the methods of science. We can make observations, formulate hypotheses, and conduct experiments

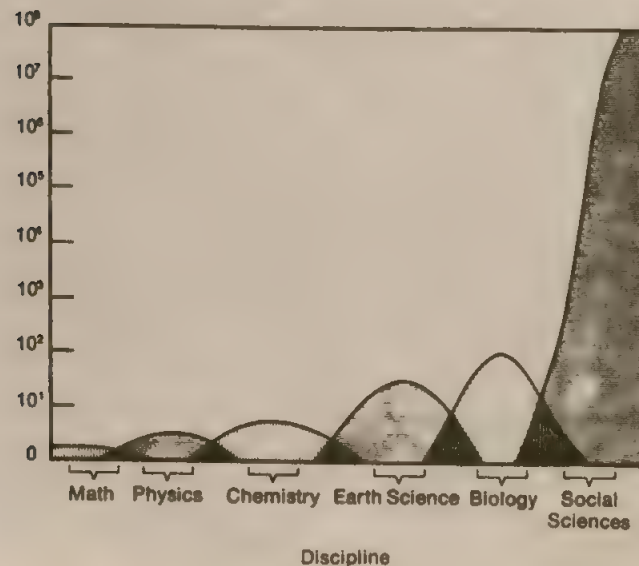


Figure 1.6 A rough estimate of the number of variables involved in the various scientific disciplines.

even if most of the variables are not subject to control. Interpretation of the results, however, is much more difficult and much more subject to disagreement. Other nonscientists use some of the methods and language of scientists. Artists experiment with new techniques and new materials. Playwrights and novelists observe life as it is before trying to express its essence in their writings. It is easy to see some of the methods of science as well as the influence of science in nearly all of the endeavors of modern men and women.

Chemistry: A Study of Matter and Energy

At the beginning of this chapter, we defined chemistry as a study of matter and the changes it undergoes. Now let's look at this subject of matter and energy a little more closely.

Since the entire physical universe is made up of nothing more than matter and energy, the field of chemistry extends from atoms to stars, from rocks to living organisms. Matter and energy are such fundamental concepts that definitions are difficult. Matter is the stuff that makes up all material things. It occupies space and has *mass*. Wood, sand, water, air, and people have mass and occupy space. These are material things. Mass is a measure of the *quantity* of matter. *Weight* is a measure of how strongly an object is attracted by the Earth. On the Earth's surface, mass is roughly equivalent to weight, and so the two terms may be used interchangeably for most purposes. In space, an astronaut, though weightless, would still have the same mass (i.e., the same quantity of matter) as on the Earth. Weight is determined by gravity; mass is invariant.

Energy often is defined as the capacity for doing work. By this definition, play involving exercise is called work. But energy is more than that. It is the basis for change in the material world. Energy appears in several forms. The source of nearly

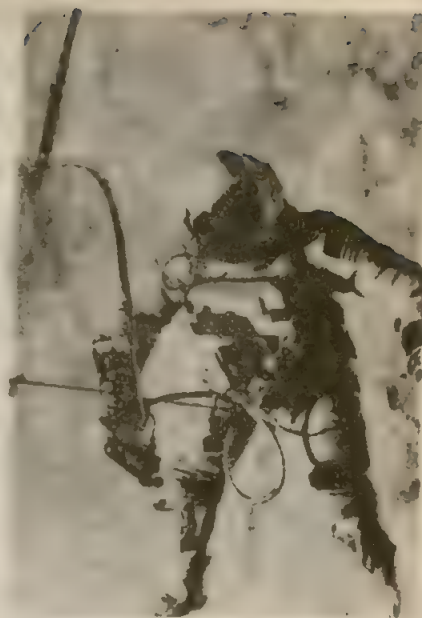


Figure 1.7 An astronaut who weighs 80 kg on Earth is weightless in space. His mass (quantity of matter) is constant, however. (Courtesy of the National Aeronautics and Space Administration.)

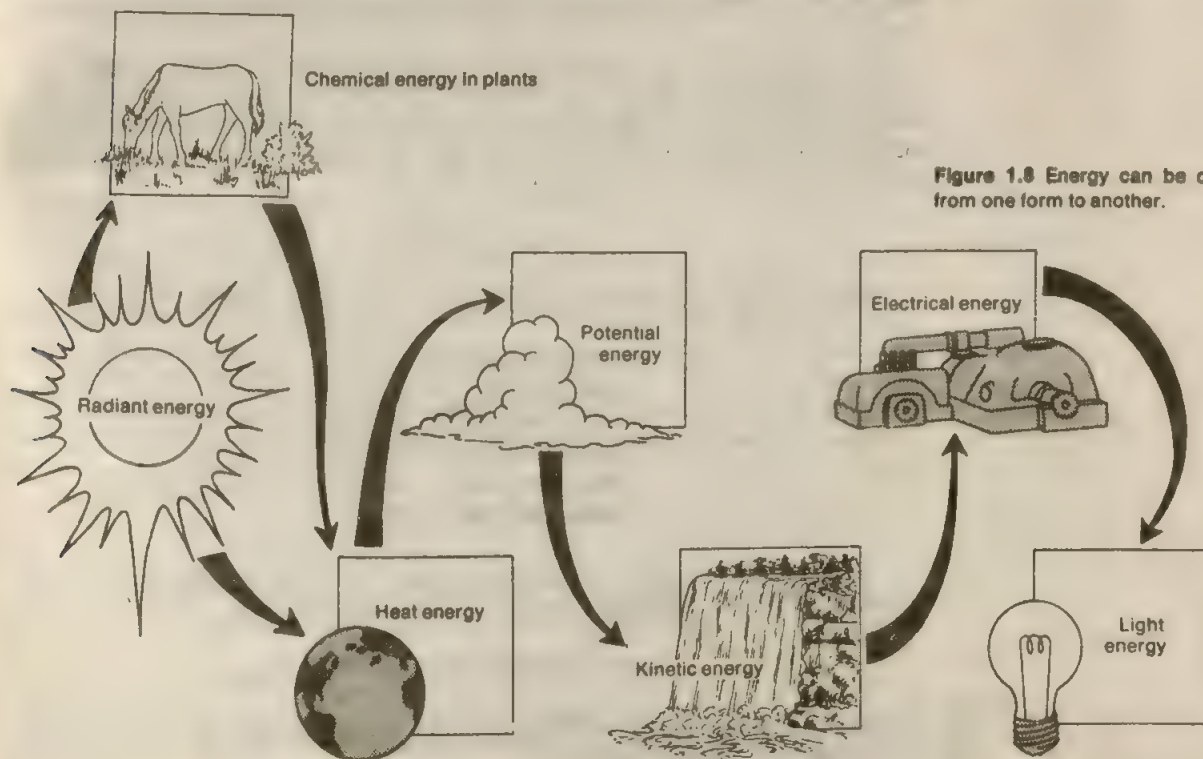


Figure 1.8 Energy can be changed from one form to another.

all of the energy on the Earth is the sun. Solar energy radiates through space. A small portion of this *radiant energy* reaches the Earth, where some of it is converted to *heat energy*. This heat causes water to evaporate and rise to form clouds. The water in the clouds has *potential energy* (energy by virtue of its position). As the water falls through the air and then flows as rivers, the potential energy is converted to *kinetic energy* (energy of motion). The kinetic energy of a flowing stream can be used to turn a turbine, which converts part of the kinetic energy to *electrical energy*. The electricity thus produced can be carried by wires to homes and factories, where it can be converted to *light energy* or to heat or back to mechanical energy.

Some of the solar energy striking the Earth's surface is absorbed by green plants, which use a complicated chemical process called *photosynthesis* to convert solar energy into *chemical energy*. The chemical energy stored by plants—today and in ages past—is used by animals and humans for food and fuel. Nearly all of the vast quantities of energy being used in our modern civilization came originally from green plants. Plants of the current age are harvested by foresters and farmers. Those of ancient ages are reaped as fossil fuels—coal, oil, and gas.

Thus, chemistry is concerned not only with matter and its changes but with the energy transformations that accompany changes in matter.

The Measurement of Matter and Energy

Accurate measurement of such quantities as mass (weight), volume, time, and temperature are essential to the compilation of dependable scientific data. A variety of systems of measurement have been used around the world. The familiar English system of feet, pounds, and quarts is now being phased out in the United States, one of the last nations to do so. Scientists find the English units cumbersome. Therefore, they have adopted on a worldwide basis an updated metric plan called the International System of Measurements, or SI (from the French *Système International*).

The beauty of SI is that only seven basic units are needed. Of those, we need only two for our purposes. The unit of length is the metre (m), and that of mass is the kilogram (kg). Other units are derived from these. For example, the unit of volume is the cubic metre (m³). A convenient unit of mass for use in the laboratory is the gram (g). A gram is a thousandth of a kilogram.

$$1 \text{ g} = 0.001 \text{ kg}$$

Other units are derived in a similar manner by the use of prefixes.

$$1 \text{ millimetre (mm)} = 0.001 \text{ m}$$

$$1 \text{ milligram (mg)} = 0.001 \text{ g}$$

$$1 \text{ kilogram (kg)} = 1000 \text{ g}$$

$$1 \text{ kilometre (km)} = 1000 \text{ m}$$

$$1 \text{ decimetre (dm)} = 0.1 \text{ m}$$

$$1 \text{ decigram (dg)} = 0.1 \text{ g}$$

The cubic metre generally is too large a unit for use in the laboratory or the kitchen. The derived SI unit often employed is the cubic decimetre.

$$1 \text{ cubic decimetre (dm}^3\text{)} = 0.001 \text{ m}^3$$

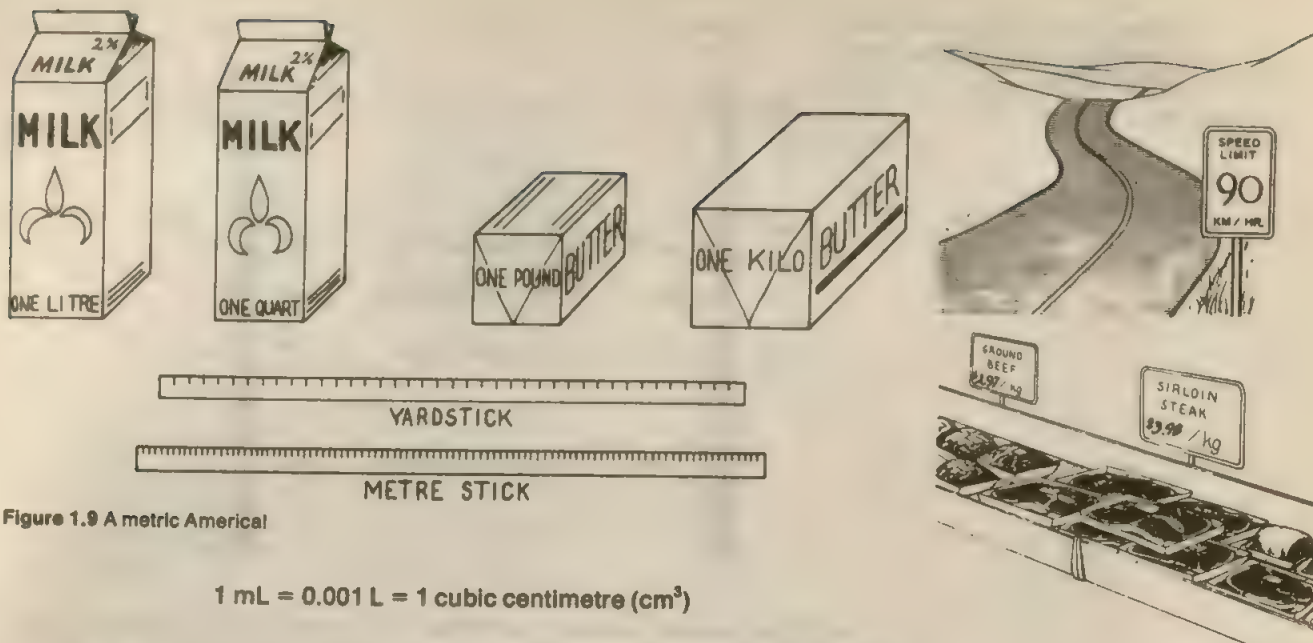


Figure 1.9 A metric American

$$1 \text{ mL} = 0.001 \text{ L} = 1 \text{ cubic centimetre (cm}^3\text{)}$$

If you are not familiar with SI, you may find the following list of approximate English equivalents helpful.

$$\begin{aligned} 1 \text{ m} &= 39.4 \text{ in.} = 1.1 \text{ yd.} \\ 1 \text{ dm}^3 &= 1 \text{ L} = 1.1 \text{ qt.} \\ 1 \text{ kg} &= 2.2 \text{ lb.} \end{aligned}$$

Scientists also use a different temperature scale. The familiar Fahrenheit scale defines the freezing temperature of water as 32 °F and the boiling point as 212 °F. For much of their work, many scientists use the Celsius scale, on which the freezing point of water is defined as 0 °C and the boiling temperature as 100 °C. The scale between these two reference points is divided into 100 equal divisions, each a Celsius degree.

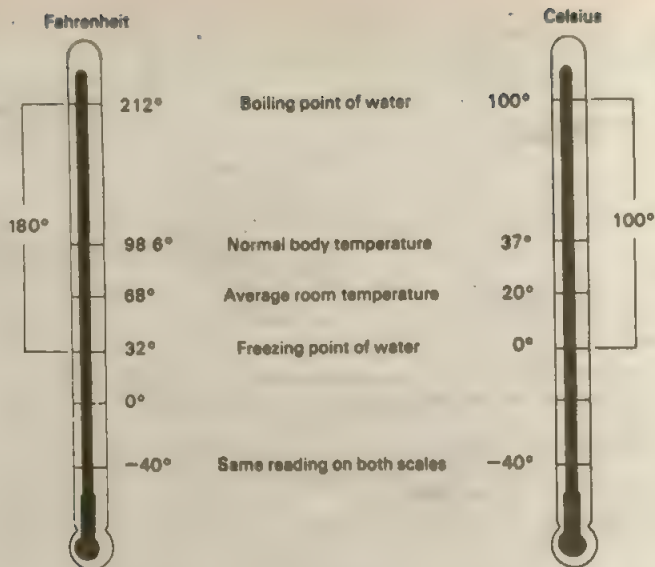
Scientists often need to measure amounts of heat energy. You should not confuse heat with temperature. Heat is a measure of quantity, that is, of *how much energy* a sample contains. Temperature is a measure of intensity, that is, of *how energetic* each individual particle of the sample is. A glass of water at 70 °C contains less heat than a bathtub of water at 60 °C. The particles of water in the glass are more energetic, on the average, than those in the tub, but there is far more water in the tub and its total heat content is greater. The SI unit of heat is the *joule* (J), but we will use the more familiar *calorie* (cal).

$$1 \text{ cal} = 4.18 \text{ J}$$

A calorie is the amount of heat required to raise the temperature of 1 g of water 1 °C. There is a more precise definition than this, but for our purposes the simpler version will do.

Physical measurement, as contrasted to counting, is never exact. A group of students could all *count* exactly 42 people in a classroom, but if they measured the width of the room, they probably would get a variety of results, depending upon the care each had taken and upon the accuracy of the measuring devices they used.

Figure 1.10 A comparison of the Fahrenheit and the Celsius temperature scales.



For those who are interested and those whose work might require it, measurement is discussed more extensively in appendix A.

The United—and the Disunited—States of Matter

Nearly everyone is familiar with matter in three of its states—solid, liquid, and gas. In our ordinary experience, there are few direct indications that matter is made up of a myriad of minute particles in constant motion. Scientists have invented an elaborate model, called the kinetic-molecular theory, to explain the properties of matter in bulk. There is ample, if indirect, evidence to support this theory.

It's a Solid!

Solid objects generally maintain their shapes and volumes no matter what their locations. Most solids are *crystalline* in nature. In some rocks, we might need a microscope to see the tiny but often beautiful crystals. Other crystals are large and can easily be seen with the unaided eye. Crystals are bounded by plane surfaces called *faces*. They split, or cleave, in certain preferred directions so that their characteristic faces and angles are retained. For example, ordinary table salt crystallizes in a cubic arrangement with square or rectangular faces. When a piece is split, the fragments have the same kind of faces as did the original piece.

These and many other properties of solids are explained in terms of a regular arrangement, or array, of the constituent atoms or molecules (figure 1.11). The particles usually are held together by strong attractive forces. There is little motion of the particles in a solid, only a gentle vibration about a fixed point in the lattice. Several crystalline solids and their structures are discussed in chapter 9.

It's a Liquid!

Liquids assume the shape of their containers (except for a generally flat surface at the top). Like solids, however, liquids maintain a fairly constant volume. Liquids flow rather readily. Water is by far the most common naturally occurring liquid. Petroleum is another familiar liquid found in nature. Thousands of liquids—such as alcohol, carbon tetrachloride, acetone, and acetic acid—have been produced artificially. Water and alcohol are *miscible*; they can be mixed in any proportion.

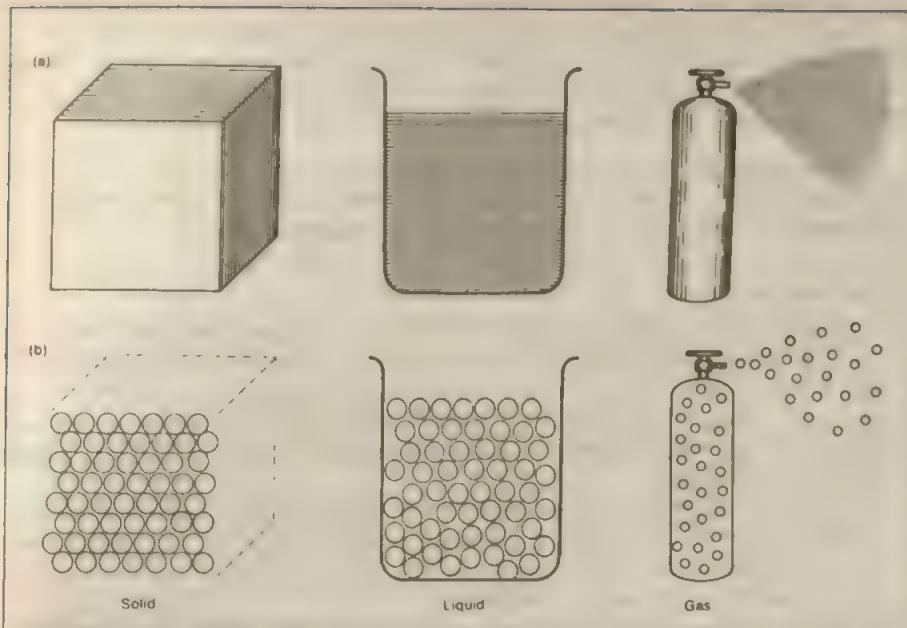


Figure 1.11 Solids, liquids, and gases. (a) Bulk properties. (b) interpretation of those properties in terms of the kinetic-molecular theory.

Alcohol will *diffuse* into water, and vice versa; the motion of the molecules eventually causes those of each liquid to be evenly distributed throughout the mixture. Oil and water are *immiscible*. If shaken together, two immiscible liquids form a cloudy mixture with tiny droplets of one suspended in the other. If allowed to stand, the droplets come together and the liquids separate into two distinct layers.

When you watch a liquid flow, imagine the particles sliding, gliding, and slipping over one another. The particles are close together, and mutual attractions are fairly strong, and yet they are free to move about. This freedom of movement explains the phenomena of flow and diffusion. Since the particles are closely spaced (see **figure 1.10**), liquids and solids are virtually incompressible.

It's a Gas!

Gases maintain neither shape nor volume. Rather, they expand to fill completely whatever container they occupy. This expansibility of gases is coupled with their easy compressibility. For example, enough air for a diver to breathe for many minutes underwater can be compressed into a steel tank that he or she can carry.

Gases also diffuse rapidly. If you opened a bottle of ammonia at one end of a room, the irritating odor would soon spread throughout the whole room. All gases mix with one another by diffusion.

Air is a mixture of several gases, chiefly nitrogen and oxygen. Natural gas is a familiar fuel in many parts of the United States. Helium is used to fill balloons. Welders use tanks of compressed oxygen and acetylene.

Although everyone knows about the existence of gases, the behavior of gases is little understood by most people. Scientists, on the other hand, find the gaseous state easier to understand than the solid or liquid state because gases can be easily manipulated. Their understanding is based on the kinetic-molecular theory of matter. The basic postulates of this theory are these.

1. All matter is composed of tiny, discrete particles called molecules.
2. These particles are in constant motion and move in straight lines.

3. The molecules of a gas are very small compared to the distances between them.
4. There is very little attraction between the molecules of a gas.
5. Molecules collide with one another. Energy is conserved in these collisions, although one molecule can gain energy at the expense of the other.
6. Temperature is a measure of the *average* kinetic energy of the gas molecules.

Since molecules are far apart, compressing a gas simply serves to move them a bit closer together. Gases diffuse rapidly because a molecule can move a long way through empty space before colliding with another molecule.

It's Supermatter

Solids, liquids, and gases are the three states of matter that are familiar to everyone. There is another state, called *plasma*, which is of increasing interest and importance. Plasma is much like a gas, except that the particles of plasma are electrically charged. The behavior of plasma is determined by electrical and magnetic forces. The outer portion of the Earth's atmosphere—the ionosphere—is largely composed of plasma.

The success of efforts to control nuclear fusion (discussed in chapter 13) depends to a great extent on the possibility of containing superhot plasma in strong magnetic fields. If indeed fusion should someday supply us with cheap and abundant energy, we might well think of plasma as supermatter.

Chemistry: Its Central Role

Chemistry is not only useful in itself, it is fundamental to other scientific disciplines as well. Biology has been revolutionized by the application of chemical principles. Indeed, an important branch of biology is called *molecular biology*. Psychology, too, has been profoundly influenced by chemistry and stands to be even more radically altered as the chemistry of the nervous system is unraveled. The social goals of better health and more and better food, housing, and clothing are dependent to a large extent on the knowledge and techniques of chemists. The recycling of basic materials—paper, glass, and metals—is primarily a matter of chemical processes. Devising new, more specific pesticides that entail less risk to useful organisms will require the application of chemical principles and skills. Chemistry is indeed a central science. There is scarcely a single area of our daily lives that is not affected by chemistry.

An understanding of chemistry is essential to an understanding of many of the problems facing society. If you want to understand how a drug or a pesticide acts, how to clean up a pollution problem, or how to avoid consumer ripoffs in cosmetics, you must know some chemistry. Much of the remainder of this book deals with such subjects. Before going on, though, let's look briefly at some of the things chemists do.

Solving Society's Problems: Applied Research

Most chemists work in the area of *applied research*. They analyze polluted soil, air, and water. They synthesize new chemical compounds for use as drugs or pesticides. They formulate plastics for new applications. They analyze foods, fuels, cosmetics, detergents, and drugs. These are examples of applied research, work oriented toward the solution of a particular problem in industry or the environment.

As a particular example, let's consider the synthesis of an antifungal drug. Many drugs are effective against bacteria, but few are useful and safe against fungal infections in humans. Seeking an effective fungal antibiotic, Rachel Brown and Elizabeth Hazen discovered nystatin, a compound effective against such fungal



Figure 1.12 Rachel Brown (left) and the late Elizabeth Hazen, codiscoverers of Nystatin, a safe fungal antibiotic. (Courtesy of Rachel Fuller Brown, Research Corporation, New York.)

infections as thrush and vaginitis. Nystatin also has been used as a fungicide in veterinary medicine and to protect fruit, and to prevent the growth of mold on art treasures in Florence, Italy, after the objects were damaged by floods. Brown and Hazen set out to find a fungicide and did so—an excellent example of applied research.

In Search of Knowledge: Basic Research

Many chemists are involved in basic research, the search for knowledge for its own sake. Some chemists work out the fine points of atomic and molecular structure. Others measure the intricate energy changes that accompany complex chemical reactions. Chemists synthesize new compounds and determine their properties. This type of investigation is called *basic research*. It is carried out for the sheer joy of unraveling the secrets of nature and discovering order in our universe.

Findings from basic research are often applied later on, but that is not the primary goal of the investigator. In fact, most of our modern technology is based on results obtained in basic research. Without this base of factual information, technological innovation would be haphazard and slow. Ominous warnings have been sounded that the United States is falling behind Germany, Japan, and other nations because it has failed to provide adequate support for basic research.

Applied research is carried on mainly by industries seeking a competitive edge with a novel, better, or more saleable product. Its ultimate aim is usually profit for the stockholders. Basic research is conducted mainly at universities and research institutes. Most of its support comes from the federal and state governments and foundations, although some of the larger industries also support basic research.

As an example of basic research that was later applied for human welfare, consider some work by Joel Hildebrand, a chemist at the University of California at Berkeley. In 1916 Hildebrand published a theoretical paper on solubility. He was able to deduce that in any liquid, helium would be found to be less soluble than any other gas. He then proposed that a mixture of helium and oxygen (rather than air, a mixture of nitrogen and oxygen) be used for deepsea diving. If air is used, nitrogen dissolves in the blood. As the diver rises toward the surface, bubbles of nitrogen separate from the blood, causing a painful affliction called the *bends*. Use of helium, which is less soluble than nitrogen in blood, prevents the bends. Use of helium-oxygen mixtures for deep diving is now commonplace. Because Hildebrand was curious about the solubility of gases in liquids, divers need not worry nearly as much about the bends as they once did.

"There are two compelling reasons why society must support basic science. One is substantial: The theoretical physics of yesterday is the nuclear defense of today; the obscure synthetic chemistry of yesterday is curing disease today. The other reason is cultural. The essence of our civilization is to explore and analyze the nature of man and his surroundings. As proclaimed in the Bible in the Book of Proverbs: 'Where there is no vision, the people perish.'"

Arthur Kornberg (1918-)
American Biochemist
Nobel Prize in Physiology and
Medicine, 1959



Figure 1.13 Joel Hildebrand, noted chemist and teacher, whose theoretical studies on solubilities led to the use of helium in deep-water diving. (Courtesy of Joel Hildebrand.)

Problems

1. List five chemical activities that you have engaged in today.
2. List three characteristics of science. Which one serves best to distinguish science from other disciplines?

3. How does technology differ from science? How are the two related?
4. What is natural philosophy?
5. What did Francis Bacon envision for us as a result of science?
6. What was the main theme of Rachel Carson's *Silent Spring*?
7. Why weren't Thomas Malthus' predictions fulfilled?
8. How does a scientific model differ from models encountered in everyday life?
9. Why can't scientific methods always be used to solve social, political, ethical, and economic problems?
10. Define each of the following terms.

a. chemistry	e. weight
b. matter	f. miscible
c. energy	g. applied research
d. mass	h. basic research
11. How do solids, liquids, and gases differ with regard to their shape and volume?
12. What is your weight in kilograms? (Remember, 1 kg = 2.2 lb.)
13. What is your height in metres? (Remember, 1 m = 3.3 ft.)
14. Would you weigh the same on the moon as you do on the Earth?
15. How many millimetres are there in each of the following?

a. 1.5 m	b. 16 cm	c. 849 μ m	d. 1 in.	e. 1 ft
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16. How many litres are there in each of the following?

a. 2056 mL	b. 47 kL	c. 0.54 dm ³	d. 5.2 qt
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17. The food Calorie is actually 1000 calories (1 kcal). In SI, we measure our food energy intake in kilojoules (1 kcal = 4.18 kJ). How many kilojoules of energy are there in a can of pop that has 165 Calories (165 kcal)?
18. Make the following conversions.

a. 15,000 mg to grams	d. 47 mL to litres
b. 0.086 g to milligrams	e. 1.5 qt. to millilitres
c. 0.149 L to millilitres	f. 18 L to quarts

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chapter 2

Atoms: Are They for Real?



Figure 2.1 Democritus. (Courtesy of the Smithsonian Institution, Washington, D.C.)

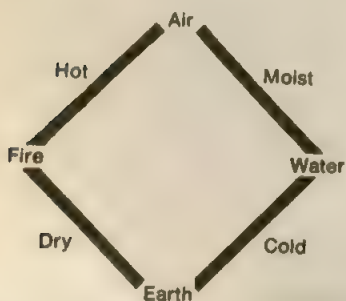


Figure 2.2 The Greek view of matter.

The word *atom* is so familiar that it seems it must always have been part of our language. Yet the birth of the concept of the atom was a difficult one, which spanned more than 2000 years. Then it took another century for our idea of the atom to mature. What we conceived of first as a hard sphere is envisioned today as a fuzzy, complicated cloud of matter.

In this chapter, we see how the concept of the atom developed and how it has changed forever the way we look at things. Who cares about atoms? You do, that's who. For all practical purposes, atoms are eternal. We can't really get rid of those we don't want. We can bury them under the ground or throw them into the sea, and sometimes we can disperse them into the air. We can combine them in different ways, and occasionally, by using a lot of energy, we can even change one kind of atom into another. But they still won't go away. Keep that in mind when you think about disposing of wastes.

Learn all you can about atoms. Remember that you and all the universe are made of atoms. So, to start our study, let's go back for a moment to ancient Greece.

Greek Atoms

In the fifth century B.C., Leucippus and his pupil Democritus strolled along an Aegean beach. Leucippus is said to have wondered aloud whether the water of the sea was continuous, as it appeared, or whether it might not be composed of tiny, separate particles like the grains of sand on the beach. From a distance, the sand appeared continuous, but closer inspection revealed that it was made up of separate grains. Leucippus could divide the water into drops and each of those into smaller ones. Was there any reason that this process could not be continued indefinitely, yielding ever smaller drops of water? This idea of endless divisibility was the prevailing view of the Greek philosophers of that time, but Leucippus, on the basis of intuition alone, concluded that there must be a limit to divisibility—that there must be ultimate particles that could not be subdivided.

Democritus, who lived from about 470 to 380 B.C., gave these ultimate particles a name. He called them *atomos*, which meant "indivisible." Democritus also

expanded the theory of matter. He believed that atoms of each element* were distinct in shape and size. Real substances were considered to be mixtures of atoms of different elements in different proportions. One substance could be changed into another by altering the proportions.

This atomic theory was expanded five centuries later by the Roman Lucretius. In a long poem, *On the Nature of Things*, Lucretius gave strong arguments for the atomic nature of matter.

These ancient theories seem remarkably modern in many respects. However, neither Greeks nor Romans had the means to determine which view of matter—atomistic or continuous—was correct. In fact, the ancients almost never experimented, preferring to reason from what they called “first principles.” Therefore, the atomistic theory remained a minority view for 2000 years. It just didn’t seem reasonable to the ancient theorists that a piece of matter could be so small that it could not be split into still smaller pieces.

The French: Experiment and Revolution

By the eighteenth century A.D., scientists were observing more carefully and measuring more accurately.

Antoine Laurent Lavoisier, a Frenchman (1743-1794), may have done more than anyone else to establish chemistry as a quantitative science. He found that when a chemical reaction was carried out in a closed system, the total weight of the system was not changed. Perhaps the most important chemical reaction that Lavoisier performed was the decomposition of the red oxide of mercury to form metallic mercury and a gas which he named oxygen. The reaction had been carried out before—by Karl Wilhelm Scheele, a Swedish apothecary (1742-1786), and by Joseph Priestley, a Unitarian minister who later fled England and settled in America—but Lavoisier was the first to weigh all reactants and products. Lavoisier was also the first to interpret the reaction correctly.

Lavoisier carried out many quantitative experiments. When coal was burned, it united with oxygen to form carbon dioxide. He also experimented with animals. When a guinea pig breathed, oxygen was consumed and carbon dioxide was formed. Therefore, Lavoisier concluded, respiration was related to combustion. In each of these reactions, he found that matter was conserved.

Lavoisier summarized his findings in these and other experiments by formulating a scientific law.† His *law of conservation of mass* holds that matter is neither created nor destroyed during a chemical change. In other words, if one weighed all the products of a reaction—solids, liquids, and gases—the total would be the same as the weight of all the original substances (called reactants).

Lavoisier also devised the first systematic way of naming chemical substances. His book *Elementary Treatise on Chemistry* provided the first unified picture of

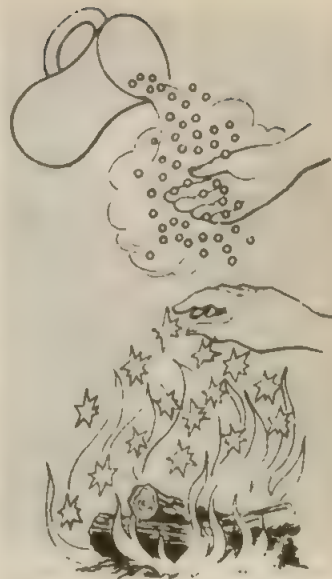


Figure 2.3 Democritus imagined that “atoms” of water could be smooth, round balls and that “atoms” of fire could have sharp edges.



Figure 2.4 Antoine Lavoisier. (Courtesy of the Smithsonian Institution, Washington, D.C.)

*The Greeks believed that there were only four elements: earth, air, fire, and water. Differences in substances were due to different proportions of these elements. The relationship between the four elements and the four “principles”—hot, moist, dry, and cold—is shown in figure 2.2.

†Scientific laws merely summarize experimental data. For example, Lavoisier found that in each of the reactions that he carried out, the total weight of products was equal to the total weight of reactants. He summarized these findings as the law of conservation of mass. This law has been verified repeatedly through the years.



Figure 2.5 Joseph Priestley. (Courtesy of the Smithsonian Institution, Washington, D.C.)

chemistry. Lavoisier is often called the father of chemistry, and his book was the first chemistry textbook. Incidentally, Lavoisier lost his head (on the guillotine) during the French Revolution, but not because of his chemical research. In those days, no one was a full-time chemist. Lavoisier had another job on the side. He was a tax collector for Louis XVI.

Joseph Priestley (1733-1804) avidly pursued chemistry as a hobby. His church in Leeds, England, was next door to a brewery. Fermentation produces large amounts of carbon dioxide, which Priestley obtained for his experiments. He discovered that carbon dioxide would dissolve in water to some extent. This carbonated water had a pleasant tart taste. Priestley is regarded by some as the father of the soda pop industry.

In 1774, Priestley visited Lavoisier in Paris. The French chemist immediately grasped the significance of the Englishman's experiments with mercury oxide. Such international exchanges of ideas have long been important to the growth of scientific knowledge. As sometimes happens, though, Lavoisier failed to acknowledge Priestley's contribution.

Priestley's liberal religious views and his sympathy for the American and French revolutions made him increasingly unpopular in England. In 1791, rioters in Birmingham set fire to his meeting house. Vandalism ruined his collection of books and scientific apparatus. Finding London also hostile, Priestley took his family to the United States in 1794. He declined a Unitarian ministry in New York and a chemistry professorship at the University of Pennsylvania to spend the last 10 years of his life writing in Northumberland, Pennsylvania. Priestley's house and laboratory in Northumberland were declared a state and national historic site for the 1974 bicentennial anniversary of his discovery of oxygen.

In 1771, Lavoisier married the 14-year-old daughter of one of his fellow tax collectors. His marriage was happy, and his wife became his eager and capable assistant in the laboratory. After Antoine's death, Madame Lavoisier edited and published many of his papers.



Figure 2.6 Robert Boyle. (Courtesy of the Smithsonian Institution, Washington, D.C.)

Scientists had by this time abandoned the Greek idea of four elements and were almost universally using Robert Boyle's operational definition, put forth over a century before. Boyle, an Englishman, in his book *The Skeptical Chymist*, published in 1661, said that supposed elements must be tested to see if they were really simple. If a substance could be broken down into simpler substances, it was not an element. The simpler substances might be elements and were so regarded until such time (if it ever came) that they in turn could be broken down into still simpler substances. On the other hand, two or more elements might combine to form a complex substance, called a compound.

Using Boyle's definition, Lavoisier included a table of elements in his *Elementary Treatise*. His table listed light and caloric (heat) as elements and included some substances we now know to be compounds. Lavoisier was the first to use modern, somewhat systematic names for the chemical elements. His table is reproduced in Figure 2.7.

But we were talking about atoms—and Frenchmen—and revolution. In 1799, Joseph Louis Proust showed that copper carbonate, whether prepared in the laboratory or obtained from natural sources, contained the same three elements—copper, carbon and oxygen—and always in the same proportions—5.3 parts of copper to 4 parts of oxygen: to 1 part of carbon. To summarize this and numerous

other experiments, Proust formulated a new law. A compound, he said, always contains elements in certain definite proportions, and in no other combinations. This generalization he called the *law of definite proportions*.

ELEMENTS

TABLE OF SIMPLE SUBSTANCES.

Simple substances belonging to all the kingdoms of nature, which may be considered as the elements of bodies.

New Names.		Correspondent old Names.
Light	. . .	Light.
Caloric	. . .	Heat.
		Principle or element of heat.
		Fire. Igneous fluid.
		Matter of fire and of heat.
		Dephlogisticated air.
Oxygen	. . .	Empyreal air.
		Vital air, or
		Base of vital air.
Azote	. . .	Phlogisticated air or gas.
		Mephitic, or its base.
Hydrogen	. . .	Inflammable air or gas,
		or the base of inflammable air.

Oxydable and Acidifiable simple Substances not Metallic.

New Names.		Correspondent old names.
Sulphur	. . .	The same names.
Phosphorus	. . .	
Charcoal	. . .	
Muriatic radical	. . .	Still unknown.
Fluoric radical	. . .	
Boracic radical	. . .	

Oxydable and Acidifiable simple Metallic Bodies.

New Names.		Correspondent Old Names.
Antimony	. . .	Antimony.
Arsenic	. . .	Arsenic.
Bismuth	. . .	Bismuth.
Cobalt	. . .	Cobalt.
Copper	. . .	Copper.
Gold	. . .	Gold.
Iron	. . .	Iron.
Lead	. . .	Lead.
Manganese	. . .	Manganese.
Mercury	. . .	Mercury.
Molybdena	. . .	Molybdena.
Nickel	. . .	Nickel.
Platina	. . .	Platina.
Silver	. . .	Silver.
Tin	. . .	Tin.
Tungstein	. . .	Tungstein.
Zinc	. . .	Zinc.

Salifiable simple Earthy Substances.

New Names.	Correspondent old Names.
Lime	Chalk, calcareous earth.
	Quicklime.
Magnesia	Magnesia, base of Epsom salt.
	Calcined or caustic magnesia.
Barytes	Barytes, or heavy earth.
Argill	Clay, earth of alum.
Silex	Siliceous or vitrifiable earth.

Figure 2.7 Lavoisier's table of elements. (From Lavoisier's *Elementary Treatise on Chemistry*, 1789. English translation, 1790.)

Proust, like Lavoisier, was a member of the French nobility. He was working in Spain, temporarily safe from the ravages of the French Revolution. His laboratory was destroyed, however, and he was reduced to poverty when the French troops of Napoleon Bonaparte occupied Madrid in 1808.

Figure 2.8 Whether synthesized in the laboratory or obtained from various natural sources, copper carbonate always has the same composition. Analysis of this compound led Proust to formulate the law of definite proportions.

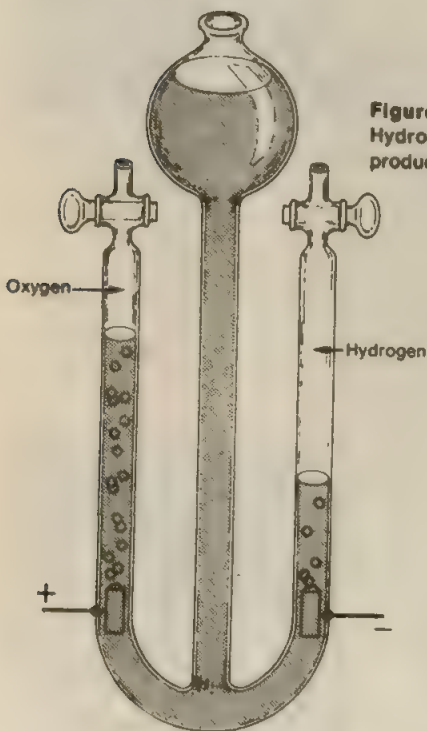
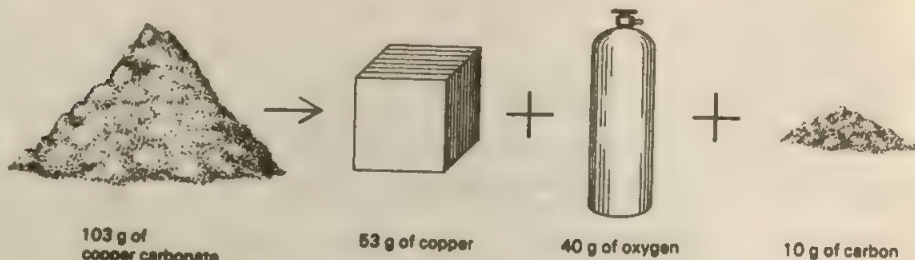


Figure 2.9 Electrolysis of water. Hydrogen and oxygen are always produced in a ratio of 2:1.

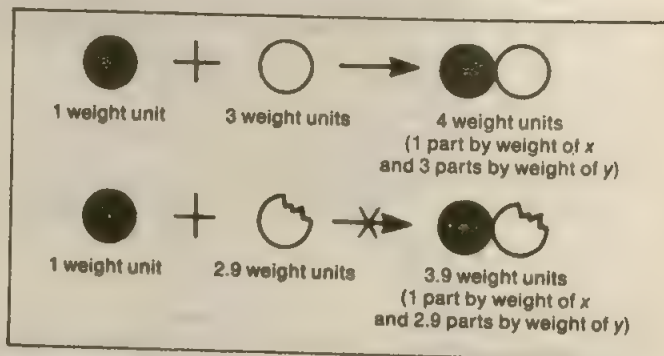


Figure 2.10 According to the atomic theory, only whole atoms can combine. The second scheme is impossible.

One of the earliest illustrations of the law of definite proportions is found in the work of a Swedish chemist, J. J. Berzelius (1779-1848). He heated 10 g of lead with various amounts of sulfur to form lead sulfide. Since lead is a soft grayish metal, sulfur is a yellow solid, and lead sulfide is a shiny black solid, it was easy to tell when all the lead had reacted. Excess sulfur was easily washed away by carbon disulfide, a liquid that dissolves sulfur but not lead sulfide. As long as he used at least 1.56 g of sulfur, he got exactly 11.56 g of lead sulfide. Any sulfur in excess of 1.56 g was left over, unreacted. If he used more than 10 g of lead with 1.56 g of sulfur, he got 11.56 g of lead sulfide, with lead left over. These reactions are illustrated in figure 2.11 and explained in figure 2.12.

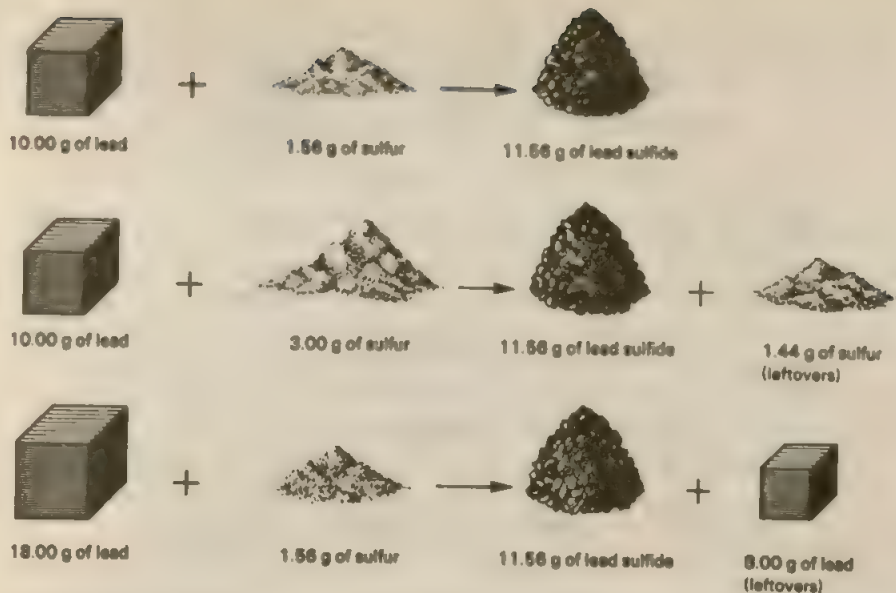


Figure 2.11 The law of definite proportions.

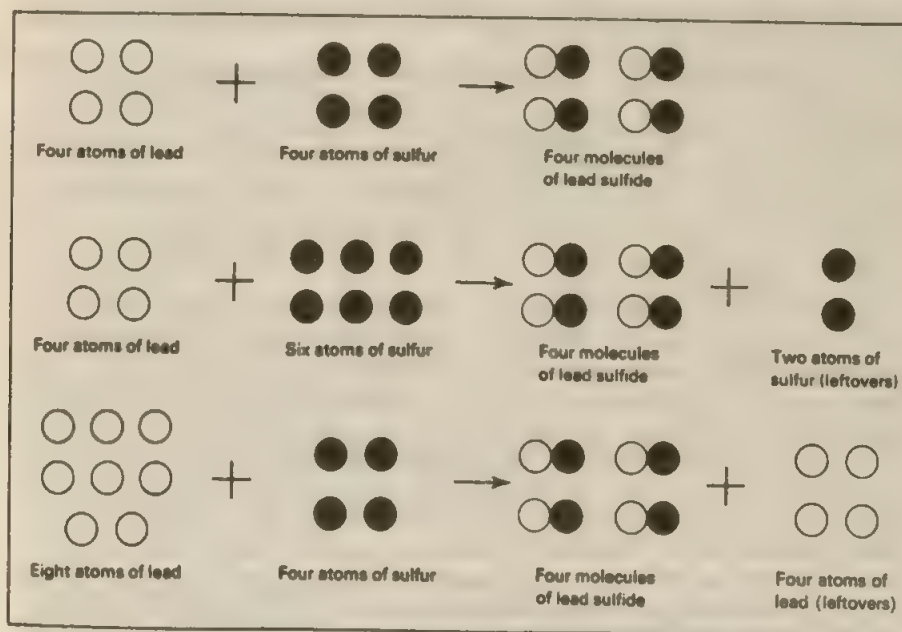


Figure 2.12 The law of definite proportions. Berzelius's experiment interpreted in terms of Dalton's atomic theory.

English Atoms

In 1783, Henry Cavendish, a wealthy and eccentric Englishman, found that water was produced when hydrogen was burned in oxygen. (It was Lavoisier, however, who correctly interpreted Cavendish's experiment and first used the modern names for hydrogen and oxygen.) In 1800, the reverse reaction was accomplished by two English chemists, William Nicholson and Anthony Carlisle. They passed electric current through water and decomposed it into hydrogen and oxygen. This they did only 6 weeks after the electric battery was invented by an Italian, Alessandro Volta. This scientific breakthrough led to very rapid develop-

Figure 2.13 The law of conservation of mass. In a chemical reaction, atoms are merely rearranged (not created or destroyed); thus, matter is conserved.

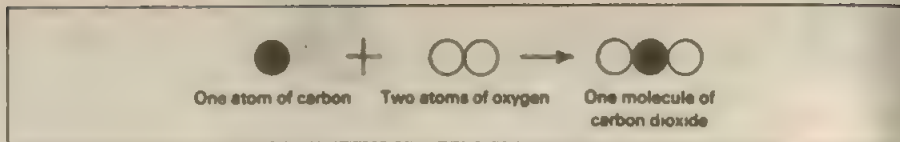
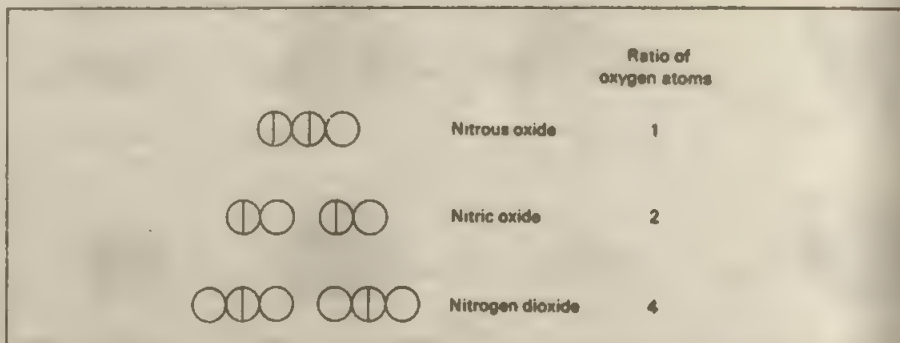


Figure 2.14 The law of multiple proportions. The amount of nitrogen is the same in each sample (two atoms). The oxygen ratio for the three compounds is 1:2:4. Although all three compounds are composed of nitrogen and oxygen atoms, they have quite different properties. Nitrous oxide, also called laughing gas, is an anesthetic. Nitric oxide is a colorless gas found in automobile exhaust. Nitric oxide is rapidly converted in air to reddish brown, poisonous nitrogen dioxide gas.



ments in chemistry and provided the death blow to the old Greek idea of water as an element, if indeed it was not already dead.

The laws promulgated by Lavoisier and Proust and the experimental successes of many others led to attempts to explain the new laws by formulating theories. If, for example, matter is continuous, why should 1 part of x always combine with 3 parts of y ? Why shouldn't 1 part of x also combine with 2.9 parts of y ? Or 3.1 parts of y ? On the other hand, if matter is assumed to be atomistic in nature, only whole atoms would combine. If one atom of y weighed three times as much as an atom of x , then the compound formed by combining x and y would have to consist of 1 part by weight of x and 3 parts of y .

John Dalton, an English schoolteacher, went through reasoning like that above. He also made a new experimental discovery. Proust had not been completely correct! Two elements might combine in more than one set of proportions. If they did, though, each set of proportions produced a different compound. For example, carbon combined with oxygen in a proportion of 3 parts of the former to 8 parts of the latter to form carbon dioxide, a gas familiar as a product of respiration and of the burning of wood or coal. But Dalton found that 3 parts of carbon would also combine with 4 parts of oxygen to form a poisonous gas that we know today as carbon monoxide. After observing the same sort of sets of proportions in other reactions, Dalton put forth his *law of multiple proportions*. In the same year, he set down his atomic theory as the only logical explanation of the two laws—the law of definite proportions and the law of multiple proportions (figures 2.13 and 2.14). Dalton arrived at his atomic theory purely on the basis of his reasoning power. His theory has been richly substantiated by subsequent experimental work and confirmed repeatedly. Experimental confirmation in recent years has often involved the use of highly sophisticated instrumentation. Formulation of so successful a theory was quite a triumph for a Quaker schoolteacher in the year 1803!

Dalton set up a table of relative weights as a most important part of his theory. In his table of atomic weights, based on hydrogen as 1, oxygen was taken to weigh 8 and carbon 6. Thus, carbon monoxide was made up of one atom of carbon combined with one atom of oxygen to give a weight ratio of 6 parts of carbon to 8 of oxygen (or 3 to 4). Carbon dioxide was made up of one atom of carbon combined with two atoms of oxygen to give a weight ratio of 6 parts of carbon to 16 parts of

oxygen (or 3 to 8). Methane, according to Dalton, was made up of one atom of carbon to two atoms of hydrogen, giving a weight ratio of 6 parts of carbon to 2 of hydrogen (or 3 to 1). We now know that methane has one atom of carbon to *four* atoms of hydrogen. In fact, many of the entries in Dalton's table of atomic weights were wrong, mainly because he assumed water to be made up of one atom of oxygen combined with one atom of hydrogen. We know today that water is made up of one atom of oxygen combined with *two* atoms of hydrogen. But, despite such inaccuracies, Dalton's atomic theory was a great success. Why? Because it served, and still serves, to *explain* a large body of experimental data. It also successfully *predicts* how matter will behave under a wide variety of circumstances. And, despite the thousands—perhaps millions—of investigations since Dalton's time, no fact of chemical behavior has ever been established that contradicts the idea of atoms.



Figure 2.15 John Dalton. (Courtesy of the Smithsonian Institution, Washington, D.C.)

John Dalton also invented a set of symbols to represent the different kinds of elements.

	Hydrogen	Oxygen	Carbon	Copper
Dalton's symbol				
Modern symbol	H	O	C	Cu

He used these in combination to represent chemical compounds.

	Water	Carbon monoxide	Carbon dioxide	Methane
Dalton's formula				
Modern formula	H ₂ O	CO	CO ₂	CH ₄

Notice that some of Dalton's formulas were incorrect. His symbolism was quite cumbersome. It was soon replaced by the modern symbols of one or two letters.

Atoms: Real and Relevant

Are atoms real? Certainly they are real as a concept, and a highly useful concept at that. Still, no one has ever seen an atom. Perhaps no one ever will.

Are atoms relevant? Much of modern science and technology—including the production of new materials and even that of pollution control—is ultimately based on the concept of atoms. We have seen that atoms are conserved in chemical reactions. Thus, material things—things made of atoms—can be recycled, for the atoms are not destroyed no matter how we use them. The one way that we might lose a material from a practical standpoint is to spread the atoms so thinly that it would take too much time and energy to put them back together again.

Consider iron atoms in a sample of hematite, an iron ore. The hematite might be converted into pig iron and then into steel and made into an automobile. After the automobile was worn out, the steel could be recovered and used again in a new automobile. Thus, the atoms could be changed from one combination to another,

but in each conversion they would be conserved. But suppose at one stage or another the iron were dissolved in sulfuric acid. The iron sulfate formed would be soluble in water. Suppose someone poured it down the drain and it eventually wound up in the ocean. The iron atoms would still be there, but they would be spread so thinly in the vast waters of the ocean that there would be no practical way to recover them.

We may conclude, then, that atoms can be recycled—provided we do not spread them too thinly.

Leucippus Revisited

Now back to Leucippus' musings by the seashore. We now know that if we kept dividing those drops of water into smaller drops, we would ultimately obtain a small particle—called a *molecule*—that was still water. If we divided that particle still further, we would obtain two *atoms* of hydrogen and one *atom* of oxygen. And if we divided those...but that is a story for another time.

Dalton regarded the atom as indivisible, as did his successors up until the discovery of radioactivity in 1895. We examine the changing concept of the atom in the next chapter.

Problems

1. Why did the theory that matter was continuous (rather than atomistic) prevail for so long? What discoveries finally refuted the theory?
2. Describe Lavoisier's contribution to the development of modern chemistry.
3. When we burn a 10-kg piece of wood, only 0.05 kg of ash is left. Explain this apparent contradiction of the law of conservation of mass.
4. When 3 g of carbon are burned in 8 g of oxygen, 11 g of carbon dioxide are formed. What weight of carbon dioxide would be formed if 3 g of carbon were burned in 50 g of oxygen? What law does this illustrate?
5. What is a scientific law? How does a scientific law differ from a governmental law?
6. What is a theory?
7. How does the Greek definition of an element differ from the modern one?
8. Explain, in terms of Dalton's atomic theory, (a) the law of conservation of mass, (b) the law of definite proportions, and (c) the law of multiple proportions.
9. When 18 g of water are decomposed by electrolysis, 16 g of oxygen and 2 g of hydrogen are formed. How much hydrogen would be formed by the electrolysis of 360 g of water? Hydrogen, from the decomposition of water, has been promoted as the fuel of the future (chapter 13). How much water would have to be electrolyzed to produce 1000 kg of hydrogen?
10. Carbon can burn in air to form either carbon monoxide or carbon dioxide, depending upon the amount of oxygen present during combustion. Using the weight ratios given on page 22, calculate how much carbon would have to be burned to produce each of these.
 - a. 140 g of carbon monoxide
 - b. 2200 g of carbon dioxide
11. The gas silane can be decomposed to give silicon and hydrogen in a ratio of 7 parts by weight of silicon to 1 part by weight of hydrogen. If the relative weight of silicon atoms is 28 when the weight of hydrogen atoms is taken to be 1, how many hydrogen atoms are combined with each silicon atom?
12. Jan Baptista van Helmont, a Flemish alchemist (1579-1644), performed an experiment in which he planted a young willow tree in a weighed bucket of soil. After 5 years, he found that the tree had gained 75 kg, and yet the soil had lost only 57 g (0.057 kg). Van Helmont had added only water to the system; hence, he concluded that the substance of the tree had come from water. Criticize van Helmont's conclusion.

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chapter 3

Atomic Structure: Images of the Invisible

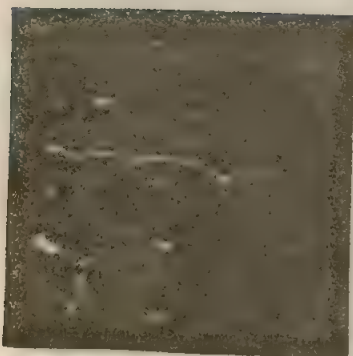


Figure 3.1 The bright spots in this photomicrograph are images of thorium atoms made by Albert Crewe with a scanning electron microscope. The thorium atoms were complexed with an organic chemical called benzenetetracarboxylic acid. (Courtesy of the Enrico Fermi Institute, Chicago.)

Dalton's concept of hard, indivisible atoms was accepted for nearly all the nineteenth century. By the beginning of the present century, however, it had become obvious that atoms were more complex. The concept of the atom changed rapidly; atoms were no longer seen as hard spheres differing only in weight; they were conceived of as being made up of component parts and of having different sizes and shapes.

Atoms are so small that they are invisible. It is impossible to see an atom in ordinary light, even with the most powerful optical microscopes. However, there are techniques for recording images of atoms. In 1970, Professor Albert Crewe of the University of Chicago announced that he had photographed images of single uranium and thorium atoms (**figure 3.1**). In 1974, Professors Gert Ehrlich and W. R. Graham at the University of Illinois in Urbana-Champaign photographed images of atoms on the surfaces of crystals (**figure 3.2**). In 1976, a group of scientists led by George W. Stroke at the State University of New York in Stony Brook photographed images showing the locations and relative sizes of tiny carbon, magnesium, and oxygen atoms in a section of a crystal (**figure 3.3**). All of these photographs were indeed remarkable achievements, but the images in them were only light spots against dark backgrounds. They did little to reveal the structures of atoms.

Why do we care about the structure of atoms? Because it is the arrangement of the parts of atoms that determines the properties of different kinds of matter. Only by understanding atomic structure can we know how atoms combine to make the many different substances in nature and, even more important, how we can modify materials to meet our needs more precisely. A knowledge of atomic structure is even essential to your health. Many medical diagnoses are based on the analysis of blood and urine. Many such analyses depend on knowledge of how the structure of atoms is changed when energy is absorbed.

Perhaps of greater immediate interest to you is the fact that your success in the study of chemistry (as well as much of biology and other sciences) will depend at least in part on your knowledge of atomic structure. Learn it now and you will be way ahead. Let's start our study of atomic structure by going back to the time of John Dalton.

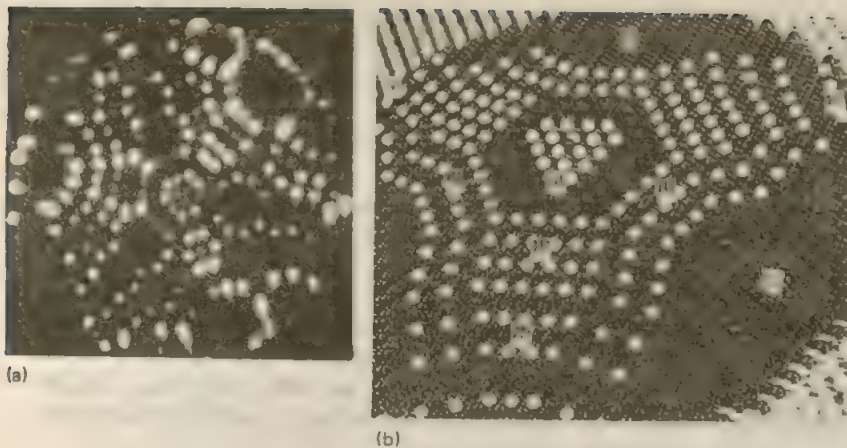


Figure 3.2 Scientists at the University of Illinois at Urbana-Champaign are using a field ion microscope to investigate atomic behavior on crystal surfaces. (a) The bright spots in the photomicrograph are atoms, magnified 10 million times, that make up the top layer of a crystal surface. (b) The bright spots in this model of a crystal surface correspond to the atoms in the photomicrograph. (Courtesy of Gert Ehrlich, University of Illinois, Urbana.)

The Nineteenth-Century Atom

Dalton, who set forth his atomic theory in 1803, regarded the atom as hard and indivisible. It wasn't long, however, before evidence accumulated to show that matter is electrical in nature. Indeed, the electrolytic decomposition of water by Nicholson and Carlisle in 1800 (chapter 2) had already indicated as much.

Sir Humphry Davy, an English chemist, built a powerful battery. With it he discovered a number of new elements. In 1807, he liberated a bright, silvery metal from molten potash (now known to chemists as potassium hydroxide). This very reactive metal he named potassium. A short time later, he produced sodium metal from molten soda (sodium hydroxide). Within a year, Davy also had produced the metals magnesium, strontium, barium, and calcium.

Sir Humphry's protégé, Michael Faraday (1791-1867), greatly extended the new science of electrochemistry. He termed the process of splitting compounds by means of electricity *electrolysis*. A compound that, when melted or taken into solution, could conduct an electric current was called an *electrolyte*. The carbon rods or metal strips inserted into a melt or a solution were named *electrodes*. One electrode, called the *anode*, bears a positive charge. The other, which carries a negative charge, Faraday called the *cathode*.

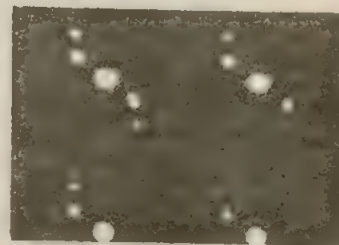


Figure 3.3 Images of magnesium, oxygen, and carbon atoms in a section of a crystal. George Stroke combined X rays, computer techniques, and holography to obtain this remarkable picture. (Courtesy of Prof. Dr. George W. Stroke, Technische Universität, Munich.)

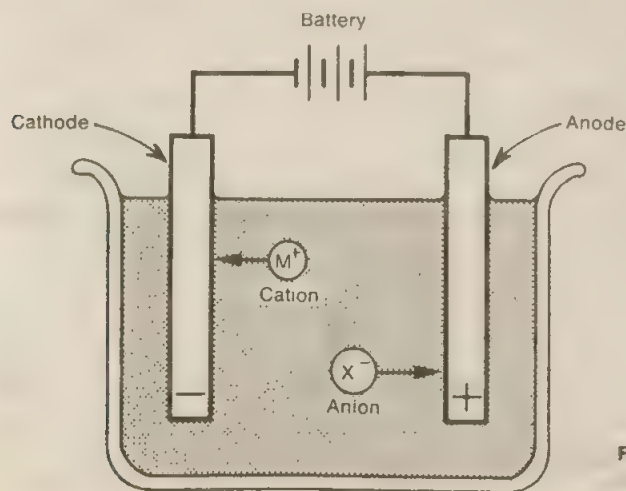


Figure 3.4 Electrolysis apparatus.

Faraday hypothesized that the electric current was carried through the melt or the solution by charged atoms, which he called *ions*. One type of ion, which bears a negative charge and travels toward the anode, he called the *anion*. The other, which has a positive charge and travels toward the cathode, he called the *cation*.

Faraday's work with solutions and melts established quite well that atoms were electrical in nature. Further detail in the structure of atoms had to wait for the development of still more powerful sources of electrical voltage and of gas discharge tubes. In fact, Faraday himself tried and failed to pass electricity through a tube that had part of the air pumped out. His vacuum just wasn't good enough.

By 1875, tubes with better evacuation were available. William Crookes passed an electric current through such a tube. The beam of current traveled in straight lines from cathode to anode. This beam was said to be composed of *cathode rays*.

But just what are these cathode rays? Streams of particles, the British scientists stoutly maintained. No, they were much more likely to be a form of light made up of

Figure 3.5 A simple gas discharge tube.

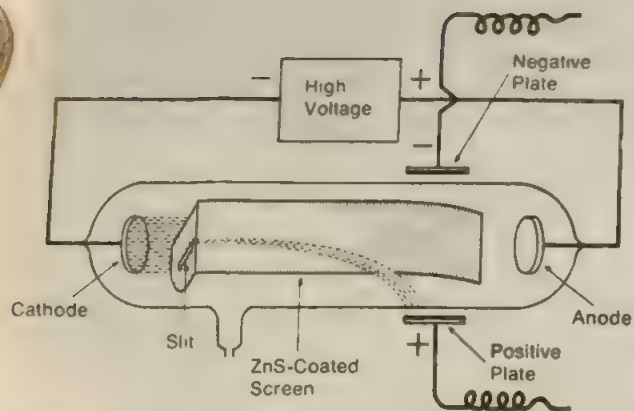
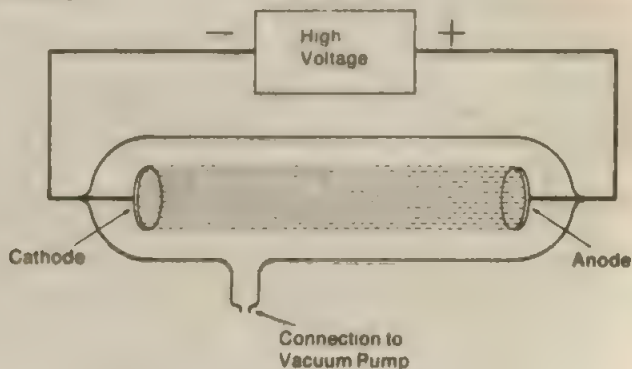


Figure 3.6 Thomson's apparatus showing deflection of an electron beam in an electric field. The screen is coated with zinc sulfide, a substance that glows when struck by electrons

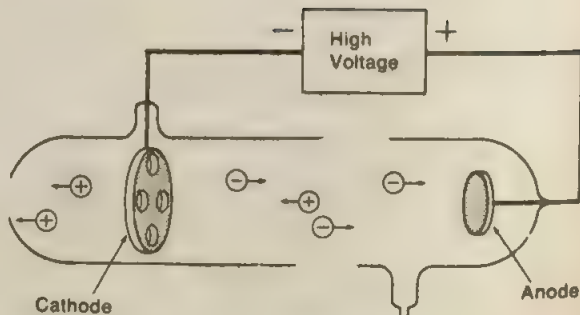


Figure 3.7 Goldstein's apparatus for studying positive particles.

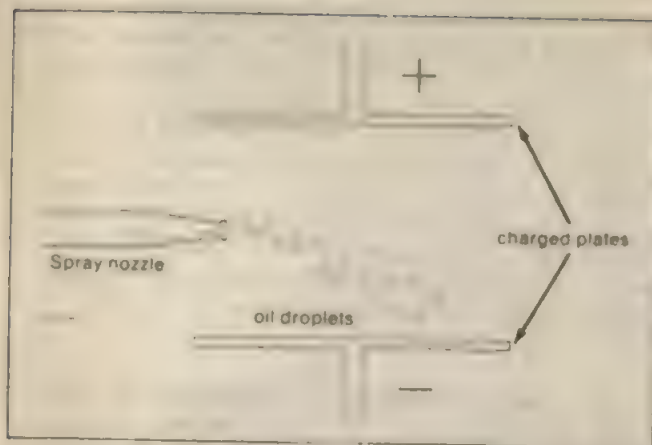


Figure 3.8 Oil-drop method for determining the charge of an electron

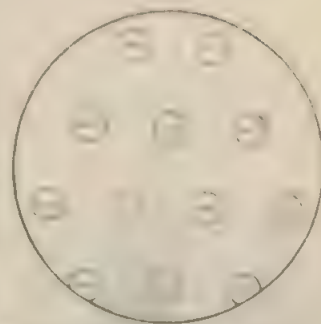


Figure 3.9 Thomson's model of the atom

waves, the Germans insisted Who was right? The answer in such cases comes—at least it should come—from experimentation, not politics. An Englishman, Joseph John Thomson, provided the answer in 1897. He showed that the cathode rays were deflected in an electric field. Since they were deflected toward the positive plate, the rays must be composed of negatively charged *particles*. Each particle carried an identical charge. The name *electron* was given to those units of negative charge. Thomson also was able to measure the mass-to-charge ratio of the cathode ray particle by determining the amount of deflection in a magnetic field of known strength. He couldn't measure either the mass or the charge separately, though. This is like determining that an apple weighs 1000 times as much as an apple seed, but not knowing the weight of the apple or its seed. Thomson won the Nobel Prize in physics in 1906.

The same type of ray was obtained regardless of the material from which the cathode was made and regardless of the gas in the tube. Thus, electrons came to be regarded as constituents of all matter.

In 1886, a German scientist named Eugen Goldstein did some experiments with gas discharge tubes that had perforated cathodes. He found that while electrons were formed and sped off toward the anode, positive rays were formed and shot in the opposite direction through the holes in the cathode. It was not until 1907, however, that a study of the deflection of these particles in a magnetic field revealed that they were of varying mass. The lightest, formed when there was a little hydrogen gas in the tube, was found later to be 1837 times as massive as an electron.

The charge of an electron was determined by an American, Robert A. Millikan, in 1909. A crude diagram of Millikan's apparatus is shown in **figure 3.8**. An atomizer is used to spray tiny droplets of oil between two charged plates. Gravity tends to cause the droplets to settle. If the droplets can be given a negative charge, however, they will be attracted upward (toward the positive plate). Movement in either direction is opposed by air resistance. X rays can be used to knock electrons loose from atoms. Some of these will adhere to oil droplets, giving the latter the desired negative charge. Through a telescope, Millikan observed the speed of droplets as they moved toward the positive plate. From the rate of rise and the magnitude of the electric field, he was able to calculate the charge on an individual droplet. The smallest possible charge on a droplet was taken to be the charge of an individual electron, a quantity that is now considered to be the basic unit of charge and that is often referred to as a charge of $1-$ (one minus). Millikan was awarded the Nobel Prize in physics in 1923.

From Millikan's value for the charge and Thomson's value for the mass-to-charge ratio, the mass of the electron was readily calculated. Electrons are extremely light particles, having a mass of only 9.1×10^{-28} gram. (If you do not understand numbers like 9.1×10^{-28} , you can find out about them in appendix B.)

Based on these discoveries, Thomson proposed a model for the atom. It was, he suggested, a solid sphere of positively charged material with negatively charged electrons stuck in it like raisins in a pudding. We could form negatively charged atoms (anions) by sticking in one or more electrons. Positively charged atoms (cations) could be formed by plucking out one or more electrons. This model served quite well to explain Faraday's electrochemical experiments and the gas discharge tube experiments, but it soon fell victim to startling new developments.

Out of Chaos: Order

Before moving on, let's take a look at a remarkable parallel development. New elements were discovered with surprising frequency. By 1830, there were 55 known elements, all with different properties and with no apparent order in these properties. John Dalton had set up a table of relative* weights in his book *A New System of Chemical Philosophy*, published in 1808. Many of Dalton's atomic weights were wrong. These were improved in subsequent years, notably by Berzelius, who published a table of atomic weights in 1828 that contained 54 elements. Except for three cases, his atomic weights are in quite good agreement with modern values.

Several attempts were made to arrange the elements in some sort of systematic fashion. The first really successful arrangement was that of Dmitri Ivanovich Mendelée'v (1834-1907), a Russian chemist. He published a *periodic table* of the elements in 1869. His table (table 3.1) arranged the elements primarily in order of increasing atomic weight, although in a few cases he placed a slightly heavier element before a lighter one. He did this to get elements with similar *chemical properties* in the same column. For example, he placed tellurium (with an atomic weight of 127.6) ahead of iodine (with an atomic weight of 126.9) because the former resembled sulfur and selenium in its properties whereas the latter was similar to chlorine and bromine.

Mendelée'v left a number of gaps in his table. Instead of looking upon these blank spaces as defects, he boldly predicted the existence of elements as yet undiscovered. Furthermore, he even predicted the properties of some of these missing elements.

In succeeding years, many of the gaps were filled in by the discovery of new elements. The properties were often quite close to those Mendelée'v had predicted. It was the predictive value of this great innovation that led to the wide acceptance of Mendelée'v's chart.



Figure 3.10 Dmitri Mendelée'v, the Russian chemist who invented the periodic table of the elements. (Reprinted with permission from Weeks, Mary E., *Discovery of the Elements*, Easton, Pa.: Chemical Education Publishing, 1968. Copyright © 1968 by the Chemical Education Publishing Company.)

* Atoms are extremely minute. During the nineteenth century, it was impossible to determine actual weights of atoms. Indirect measurements, however, could indicate their relative weights. Dalton's atomic weights were based on an atomic weight of 1 for hydrogen. As more accurate atomic weights were determined, this standard was replaced by one in which oxygen was assigned a value of 16.0000. This latter standard survived until the middle of the present century, when it was replaced by a slightly more logical one based on an isotope (chapter 4) of carbon. Adoption of this new standard caused very little change in the relative weights.

These relative weights of atoms usually are expressed in terms of *atomic mass units* (amu).

Table 3.1
Mendeléeev's periodic table, as published in the *Journal of the Russian Chemical Society* (1869)

			Ti = 50	Zr = 90	? = 180
			V = 51	Nb = 94	Ta = 182
			Cr = 52	Mo = 96	W = 186
			Mn = 55	Rh = 104.4	Pt = 197.4
			Fe = 56	Ru = 104.4	Ir = 198
		Ni =	Co = 59	Pt = 106.5	Os = 199
			Cu = 63.4	Ag = 108	Hg = 200
H = 1	Be = 9.4	Mg = 24	Zn = 65.2	Cd = 112	
	B = 11	Al = 27.4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210
	O = 16	S = 32	Se = 79.4	Te = 128?	
	F = 19	Cl = 35.5	Br = 80	I = 127	
Li = 7	Na = 23	K = 39	Rb = 85.4	Cs = 138	Tl = 204
		Ca = 40	Sr = 87.4	Ba = 137	Pb = 207?
		? = 45	Ce = 92		
		?Er = 56	La = 94		
		?Yt = 60	Di = 95		
		?In = 75.6	Th = 118?		

This modern periodic chart (inside front cover) has been extended until it contains over 100 elements. Chemists still use it to predict the properties of new elements.*

* In 1971, a team of six British scientists claimed to have produced element number 112. They confidently placed it in Group IIB, just below mercury (Hg, element number 80) because its properties resembled those of mercury. This claim has not been verified by other investigators and so is not accepted by the world community of scientists.

Serendipity in Science

Let's return now to the structure of the atom. Let's also look at a little scientific serendipity. A lot of scientific discoveries often are described as happy accidents. Have you ever wondered why these accidents always seem to happen to scientists? It is probably because scientists are trained observers. The same accident could happen right before the eyes of an untrained person and go unnoticed. Or, if it were noticed, its significance might not be grasped.

Two such happy accidents occurred in the last years of the nineteenth century. In 1895, a German scientist, Wilhelm Konrad Roentgen, was working in a dark room, studying the glow produced in certain substances by cathode rays. To his surprise, he noted this glow on a chemically treated piece of paper some distance from the cathode ray tube. The paper even glowed when taken to the next room. Roentgen had discovered a new type of ray that could travel through walls! The rays were given off from the anode whenever the cathode ray tube was operating. With



Figure 3.11 An early example of the use of X rays in medicine. Prof. Michael Pupin, of Columbia University, made this X ray in 1896 to aid in the removal by surgery of gunshot pellets (the dark spots) from the hand of a patient. (Courtesy of Burndy Library, Norwalk, Conn.)

seeming lack of imagination, Roentgen called the mysterious, penetrating rays X rays.

As is often the case when an exciting new discovery is made, many other scientists began to study the new phenomenon. One, Antoine Henri Becquerel, a Frenchman, was studying fluorescence. Certain chemicals, when exposed to strong sunlight, continued to glow even when taken into a dark room. Was this phenomenon related to X rays? He wrapped photographic film in black paper, placed a few crystals of the fluorescing chemical on top of the paper, and placed it in strong sunlight. If the glow were ordinary light, it would not pass through the black paper. If, on the other hand, the glow were similar to X rays, it would pass through the black paper and fog the film.

Before Becquerel found out very much about fluorescence, he accidentally made an important discovery. He was testing a crystal of a uranium compound. When placed in sunlight, it fogged the photographic film. During several cloudy days when work in sunlight was impossible, Becquerel prepared samples and placed them in a drawer. To his great surprise, the photographic film was exposed even though the uranium compound had not been exposed to sunlight. Further experiments showed that this radiation had no connection with fluorescence but was a characteristic of the element uranium.

Right away many other scientists began to study this newly discovered type of radiation. One, Marie Skłodowska Curie, gave this new phenomenon the name *radioactivity*. Marie Skłodowska was born in Poland in 1867. She went to Paris to work for her doctor's degree in mathematics and physics. There she met and married Pierre Curie, a French physicist of some note. Often with the help of her husband, she discovered a number of new radioactive elements, including radium. Pierre Curie was killed in a traffic accident in 1906, 3 years after he, his wife, and Becquerel were awarded the Nobel Prize in physics. Marie Curie continued to work with radioactivity, winning the Nobel Prize for chemistry in 1911. She died in 1934 of pernicious anemia, perhaps brought on by deprivation, hard work, and long exposure to radiation from the materials with which she had worked.

A New Atom for a New Century

It was soon realized that the radiation emanating from uranium and thorium was of three types. When passed through a strong magnetic field, the second type was deflected mildly in a direction opposite to the first, and the third type was not deflected at all. These types of radiation were named *alpha* (α), *beta* (β), and *gamma* (γ) rays, respectively, by Ernest Rutherford, a New Zealander working at McGill University in Montreal. The alpha rays were shown to have a mass four times that of the hydrogen atom and a charge twice that of the electron and opposite in sign. Alpha particles are, therefore, identical to helium nuclei. Beta rays were shown to be identical to cathode rays; that is, they were shown to be streams of electrons. Electronic charge is usually assigned a value of $1-$. Thus, alpha particles have

Table 3.2
Types of radioactivity

Name	Symbol	Mass (in atomic mass units)	Charge
Alpha	α	4	$2+$
Beta	β	$\frac{1}{1837}$	$1-$
Gamma	γ	0	0



Figure 3.12 Marie Skłodowska Curie. (Courtesy of Culver Pictures.)

charges of $2+$. The third type of ray, called gamma, was shown to be very much like X rays, only more penetrating. These properties are summarized in table 3.2.

Rutherford soon used the positively charged alpha particles to make an important discovery. He placed some highly radioactive material in a lead-lined box with a tiny hole. Most of the alpha particles were absorbed by the lead, but those escaping through the hole comprised a narrow stream of very high energy particles. This apparatus, then, could be aimed like a gun at some target (figure 3.14).

One target that Rutherford selected was a thin piece of gold foil. With J. J. Thomson's model of the atom in mind, Rutherford expected most of the alpha particles to be deflected only slightly by the positive charge in the atom. (Recall that Thomson's "raisin pudding" model had the positive charge spread throughout the

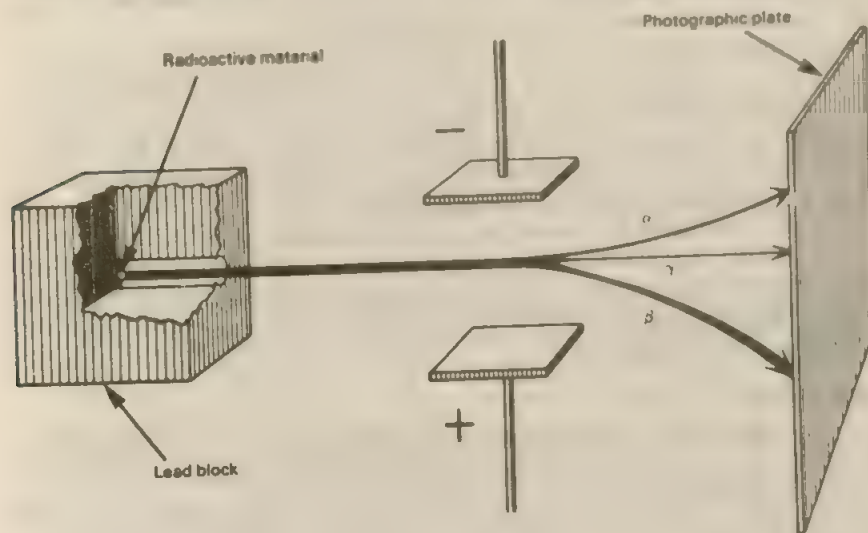


Figure 3.13 Behavior of radioactive rays in an electric field.

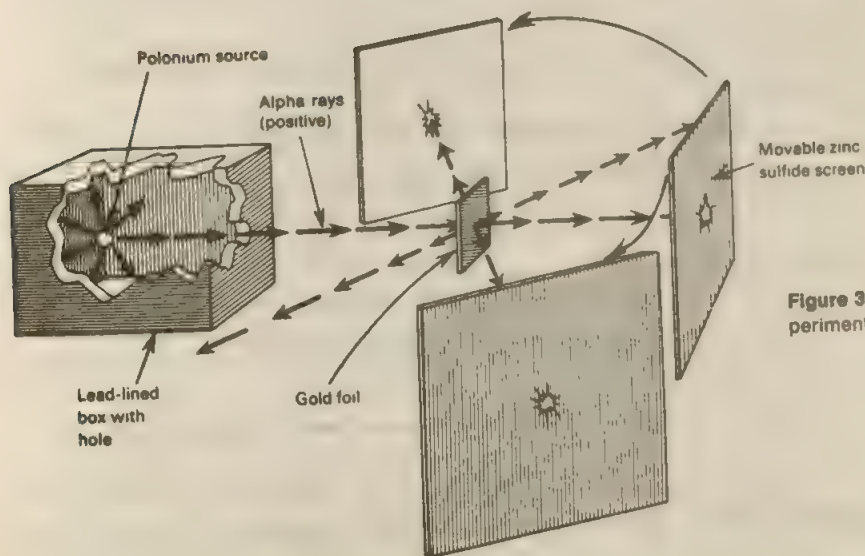


Figure 3.14 Rutherford's gold foil experiment.

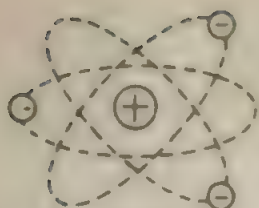


Figure 3.15 Rutherford viewed the atom as a positively charged nucleus surrounded by negatively charged electrons

atom.) Much to his surprise, Rutherford found that most of the alpha particles went through the foil, which was about 2000 atoms thick, without being deflected at all. A few of the particles, however, were deflected very sharply, obviously by a very powerful force. Since very few alpha particles were deflected, Rutherford concluded that atoms are largely empty space. Most of the mass and all the positive charge are concentrated in a very small volume, which he named the *nucleus*.

A summary of some of the more important contributions to the development of the nuclear theory of the atom is given in **table 3.3**. Any such summary must be sketchy and incomplete. Numerous, if somewhat less important, contributions by a variety of scientists are necessarily left out. It is seen, however, that the accomplishments of any one investigator depend to a great extent on those of his or her predecessors. An experimental or theoretical breakthrough in one area often led to important discoveries in another. And some of these landmark contributions were due to "accidental" discoveries by trained investigators.

Rutherford's nuclear theory of the atom, set forth in 1911, was revolutionary indeed. He postulated that all the positive charge and virtually all the mass were concentrated in the tiny, tiny nucleus. The negatively charged electrons, he said, had virtually no mass and yet they occupied nearly all the volume of the atom. By analogy, if the nucleus were the size of a pea, the surface of the atom would be several city blocks away. If the atom were the size of a baseball, the nucleus would be invisibly small and yet it would contain virtually all the mass of the baseball.

The nuclear theory led to a new interpretation of chemical reactions. The nucleus, surrounded by a cloud of electrons, remained unchanged during a chemical reaction. Electrons could be removed from or added to the surface of the atom, thus forming positive or negative ions.

The Nucleus

In 1914, Rutherford suggested that the smallest positive ray particle (i.e., that which is formed when there is hydrogen gas in the Goldstein apparatus) be taken as the unit of positive charge in the nucleus. These units, later called *protons*, were shown to have nearly the same mass as a hydrogen atom but a charge equal in magnitude to that of the electron. Except for hydrogen atoms, however, atomic nuclei were found to be heavier than would be indicated by the number of positive

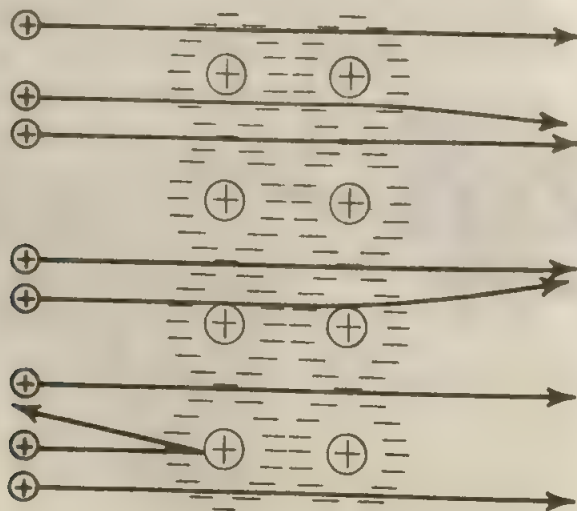


Figure 3.16 Model explaining the results of Rutherford's experiment.

charges (number of protons). For example, the helium nucleus was found to have a charge of $2+$ but a mass *four* times that of hydrogen. This excess weight puzzled scientists until 1932, when the English physicist James Chadwick discovered a

Table 3.3
A summary of some of the more important contributions leading to Rutherford's nuclear theory of the atom

<i>Investigator(s)</i>	<i>Type of Experiment</i>	<i>Contribution</i>
Nicholson and Carlisle (1800), Davy (1807-1808) Faraday (mid-1800s)	Conducted various experiments with electrolysis.	Found matter to be electrical in nature; found that current was carried through a molten salt or solution by charged atoms called <i>ions</i> .
Crookes (1875)	Passed electric current through partially evacuated glass tubes.	Discovered cathode rays.
J. J. Thomson (1897)	Deflected cathode rays in an electric field.	Found cathode rays to be made up of electrons; determined mass-to-charge ratio of electrons.
Goldstein (1886)	Experimented with gas discharge tubes with perforated cathodes. (Goldstein's experiments were not correctly interpreted until 1907, when these positive rays were deflected in an electric field.)	Discovered positive particles of varying mass in gas discharge tubes; thus, saw matter to be composed of negative particles of constant mass and charge (electrons) and positive particles of much greater, varying mass.
Millikan (1909)	Conducted experiments with oil drops.	Determined charge of electrons.
Roentgen (1895)	Studied glow produced by cathode rays.	Accidentally discovered X rays.
Becquerel (1896)	Studied possible relationship between fluorescence and X rays.	Accidentally discovered radioactivity.
Rutherford (1899)	Deflected radioactive rays.	Discovered three types of rays, which he named alpha (α), beta (β), and gamma (γ).
Rutherford (1911)	Bombarded gold foil with alpha particles.	Developed the nuclear theory of the atom.

"Science has its cathedrals, built by a few architects and many workmen." Gilbert Newton Lewis, American chemist (1875-1946).

particle with about the same mass as a proton but with *no* electrical charge. Thus the helium nucleus was made up of two protons and two *neutrons*, giving it a relative mass of about 4.

With the discovery of the neutron, the list of building blocks that we will need for constructing atoms is complete. The properties of these particles are summarized in **table 3.4**.

All atoms, except hydrogen (which has only a proton for a nucleus), have a tiny nucleus composed of protons and neutrons and have electrons somewhere outside their nuclei.

Table 3.4
Subatomic particles

Particle	Symbol	Mass (in atomic mass units)	Charge	Location in Atom
Proton	p	1	1+	Nucleus
Neutron	n	1	0	Nucleus
Electron	e	$\frac{1}{1837}$	1-	Outside nucleus

Electronic Structure: The Danish Modern Atom

When white light from an incandescent lamp is passed through a prism, it is separated into a continuous spectrum, or rainbow, of colors (**figure 3.17**). On the other hand, if the light from a flame containing a volatile salt is passed through a prism, only narrow colored lines are obtained (**figure 3.18**). Each line corresponds to light of a definite energy, indicating that atoms can only radiate light of certain energies. The line spectrum of each element is characteristic and can be used to identify the element (**figure 3.19**). Scientists have used line spectra to determine the chemical makeup of stars and the atmospheres of planets.

The first satisfactory explanation of line spectra was set forth by a Danish physicist, Niels Bohr, in 1913. He made the revolutionary suggestion that electrons cannot have just any energy but only certain specified values; that is, the total energy of an electron is *quantized*. An electron, by absorbing a *quantum* of energy (for example, when atoms of the element are heated in a flame), is elevated to a higher energy level. By giving up a quantum of energy, the electron may return to a lower

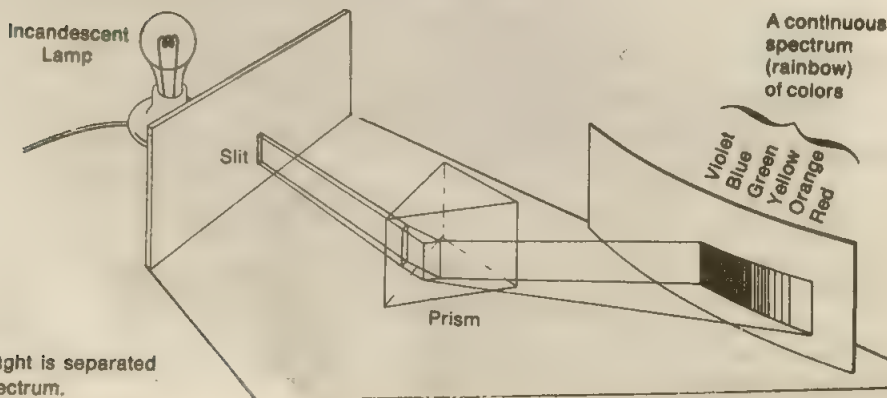


Figure 3.17 White light is separated into a continuous spectrum.

In a crude way, the color of a flame can be used to identify an element. Sodium salts give a persistent yellow color. Potassium salts give a fleeting lavender color. Barium salts give a yellow-green color; copper salts, a bright green. There is a story, perhaps apocryphal, of a worker in a chemical plant who suspected that food left on the plate wound up in the next day's soup. He put lithium chloride on his leftovers one day. Liquid from the soup the next day gave the telltale brilliant red flame test for lithium, confirming his suspicion.

energy level (figure 3.20). The energy given off, having only certain specified values, shows up as a line spectrum. An electron moves *instantaneously* from one energy level to another.

Figure 3.18 A line spectrum.

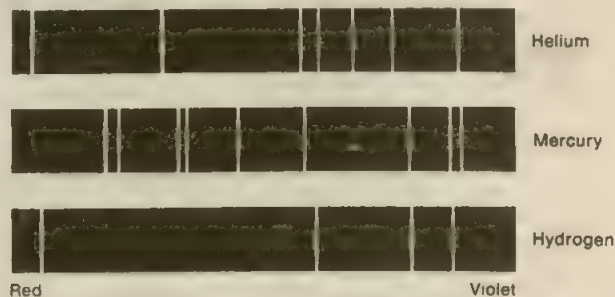
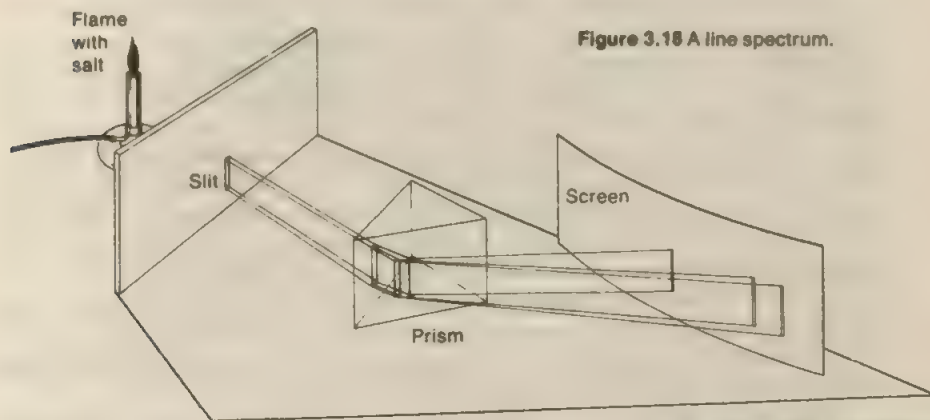


Figure 3.19 Characteristic line spectra of some elements.

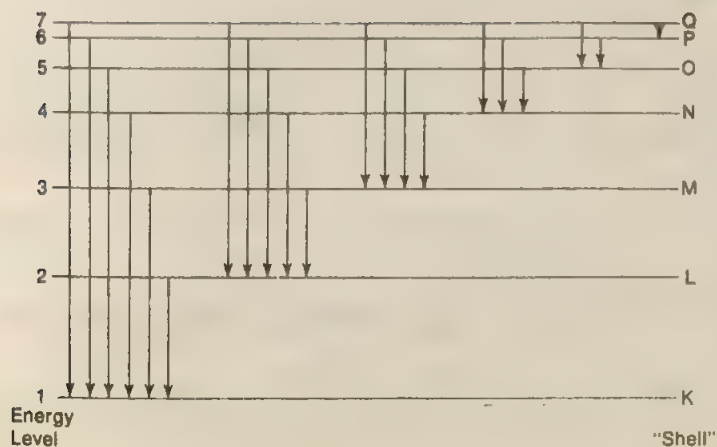


Figure 3.20 Possible electron shifts between energy levels in atoms to produce the lines found in spectra. Not all the lines are in the visible portion of the spectrum. Energy levels are sometimes called "shells" and are lettered as indicated on the right side of the figure.



Figure 3.21 Bohr visualized the atom as planetary electrons circling a nuclear sun.

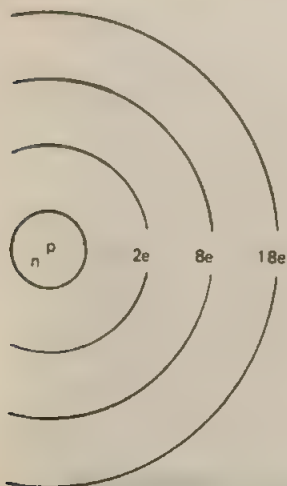


Figure 3.22 A shorthand drawing of a Bohr atom.

An analogy would be that of a person on a ladder. The person can stand on the first rung, the second rung, et cetera, but is not able to stand between rungs. From one rung to another, the person's potential energy (energy due to position) changes by definite amounts, or quanta.

The energy levels in an atom are numbered, starting with the lowest as 1, the next lowest as 2, et cetera. The maximum number of electrons in a given level is given by $2n^2$. For the first energy level ($n = 1$), the maximum population is $2(1)^2$, or 2. For the second energy level ($n = 2$), the maximum number of electrons is $2(2)^2$, or 8. For the third level, the maximum is $2(3)^2$, or 18.

Energy Levels and the Periodic Table

The properties of atoms depend mainly on the number of electrons in the outermost energy level. Imagine building up atoms by adding one electron to the proper shell as protons are added to the nucleus. For hydrogen (H), with a nucleus of only one proton, the one electron goes into the first energy level (the K shell). For helium (He), with a nucleus of two protons (and two neutrons), the two electrons both go into the first energy level. Two electrons is the maximum population of the first energy level; thus, it is filled in the helium atom. With lithium (Li), the third electron goes into the second energy level. This process of buildup is continued until the second energy level is filled with eight electrons in the neon (Ne) atom. This buildup is diagrammed in **figure 3.23**. Sodium (Na), with one electron in the outermost energy level, is similar to lithium in its properties. Helium and neon, having filled outer shells, also are similar in that both are inert. We could continue to build atoms (in our imagination) in this manner and, with a few modifications, build up the entire periodic chart of elements (inside front cover).

The modern periodic chart differs from that of Mendeléeve in that the elements are arranged according to *atomic number*. This number gives the number of protons in the nucleus and (for a neutral atom) the number of extranuclear electrons. The



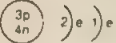
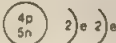
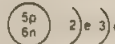
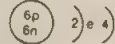




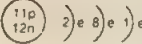
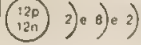
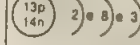
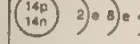
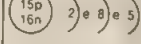
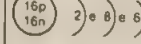
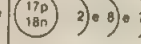
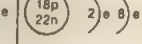
 H							 He
 Li	 Be	 B	 C	 N	 O	 F	 Ne
 Na	 Mg	 Al	 Si	 P	 S	 Cl	 Ar

Figure 2.22 Shell diagrams of the first 18 elements.

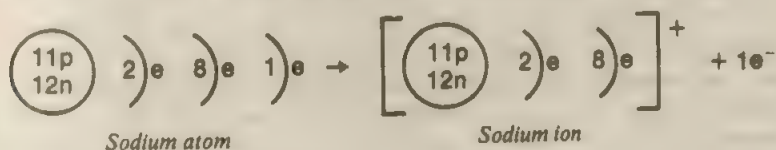
Figure 3.23 Shell diagrams of the first 18 elements.

number of neutrons* can be calculated by subtracting the atomic number from the atomic weight, the latter being rounded to the nearest whole number. For example, the number of neutrons in the sodium nucleus is $23 - 11 = 12$.

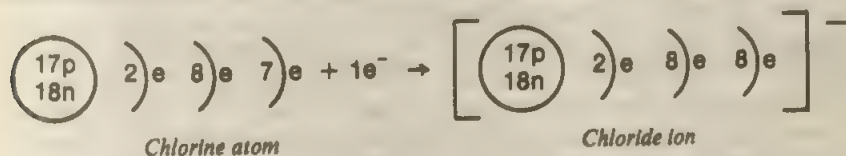
Note that the filling of an energy level corresponds to a period (a horizontal row) of the periodic chart. Also note that atoms in the same group or family (those in one vertical column) have the same number of electrons in the outermost energy level. For example, hydrogen, lithium, and sodium each have one electron in the outermost energy level. Likewise, oxygen and sulfur each have six electrons in the outer level.

The Bohr Model and Experimental Observation

The Bohr model for the atom can be used to explain a great deal more than line spectra of elements. The electrolysis experiments of Nicholson and Carlisle and of Davy and Faraday can be interpreted on the basis of the existence of *ions*. Some atoms lose electrons from the outer shell to form positive ions, and other atoms accept additional electrons in the outer shell to form negative ions. For example, the sodium atom can give up an electron to form a positive sodium ion.



Chlorine atoms, on the other hand, can accept electrons to form negative ions.



It is ions such as these that conduct electricity during the process of electrolysis.

In gas discharge tube experiments, cathode rays are simply the electrons that have been stripped off atoms of the gas by the high electrical potential. The positive rays observed by Goldstein were composed of the ions left behind when electrons were removed from the atoms of the gas.

The X rays observed by Roentgen also can be explained in terms of the Bohr model. High energy cathode rays strike electrons in the inner energy levels of atoms, dislodging them from the atom. Outer electrons then cascade down into the vacant inner levels, giving up energy in the form of X rays as they do so.

The alpha, beta, and gamma rays mentioned in this chapter originate in the atomic nucleus, not from among the orbital electrons. These forms of radiation are discussed further in chapter 4.

The existence of positive and negative charges in atoms also suggests a possible

*Atoms of most elements have varying numbers of neutrons in the nucleus. This results in the existence of isotopes—atoms of the same element having different weights. The procedure described here works for the most common isotopes of elements of the first three periods. Isotopes are discussed in more detail in the next chapter.

explanation for the binding of atoms into crystalline structures and into molecules, as we shall see in chapter 5.

Bohr's model was based on the laws of planetary motion that had been set down by the Danish astronomer Johannes Kepler three centuries before. Bohr imagined the electrons to be orbiting about the nucleus much as the planets orbit the sun. One shortcoming of such a theory was that a moving charge—the electron—should radiate energy continuously. Obviously, this was not the case, for atoms give only line spectra.

Another failure of the Bohr theory was that it could not satisfactorily account for the spectra of atoms more complicated than hydrogen. Thus, physicists and chemists went on to develop still more sophisticated—and more accurate—models for the atom. But Bohr had revolutionized our thinking about the structure of the atom, and many of his ideas are still useful today.

The Modern Mathematical Atom

Quantum theory has become highly mathematical. Electrons are treated as waves, and their location is treated only in terms of probabilities.

It was the young French physicist Louis de Broglie who first suggested (in 1924) that the electron should have wavelike properties. In other words, de Broglie said that a beam of electrons should behave very much like a beam of light. Since Thomson had proved (in 1897) that electrons were particles, this suggestion that they be treated as waves was hard to accept. Nevertheless, de Broglie's theory was experimentally verified within a few years. Electron microscopes, which make use of the wave nature of electrons, now are found in many scientific laboratories.

A model of the atom based on the wave nature of the electron was developed during the late 1920s, principally by the German physicist Erwin Schrödinger. Fundamental to the modern picture of the atom are elaborate equations, like that proposed by Schrödinger in 1927, which describe the properties of the electron waves in atoms. Solutions to these equations are called wave functions, or *orbitals*. These wave functions can be manipulated to provide a measure of the probability of finding an electron in a given volume of space. The definite, planetary orbitals of the Bohr atoms are abandoned* in favor of charge clouds—volumes of space in which the electrons move.

The calculations involved in the solution of wave equations are complicated and time-consuming. We don't need to be able to do these elaborate calculations, however, in order to use some of the results of quantum mechanics. For example, a plot of the electron probability distribution of an electron in the lowest energy level always has a spherical symmetry. Such orbitals are designed as *1s* orbitals.

The first two electrons in the second energy level also have spherical symmetry. These wave functions are called *2s* orbitals. The next six electrons of the second energy level go into three orbitals that are dumbbell shaped. These are designated *2p* orbitals. Representations of these charge clouds are given in figure 3.25. Strictly speaking, these orbitals would have to be infinite in size to account for an electron with 100% certainty. For convenience in representing orbitals, however, an outline drawing is used to indicate a 95% probability of finding the electron within the volume so outlined (figure 3.26).

$$E(\psi) = -\frac{h^2}{8\pi^2 m} \nabla^2 \psi + V(\psi)$$

Schrödinger's equation



Figure 3.24 Erwin Schrödinger, the German physicist who developed mathematical equations for the structure of atoms in which electrons were treated as waves. (Courtesy of the Nobel Institute, Stockholm.)

*It is interesting to note, however, that the figure given by Bohr for the radius of the first orbit (52.9 picometres (pm)) is the same as the most probable distance from the nucleus of an electron in the first energy level—as revealed by wave mechanical calculations.

An orbital can be occupied by one electron or by two paired electrons. Thus, there can be at most two 1s electrons, two 2s electrons, and six 2p electrons in an atom.

The mathematical picture of the atom has grown quite abstract in recent years. The atomic physicist sometimes seems to say that only the mathematics, not the atom, is real.

For our purposes, we use whatever model is most helpful in understanding a particular concept. In trying to understand the behavior of gases, chemists often use Dalton's hard, indivisible (billiard ball) model. In discussing how atoms combine, we use the Bohr model for the most part. To explain the shape of molecules (very important in explaining the action of drugs, for instance), we use an extension of the Bohr theory called the *valence shell electron pair repulsion (VSEPR) theory* for the most part. A model or a theory is used to explain phenomena. When a better model or theory is invented, the older one is discarded or pushed into a secondary role.

Problems

- What did each of the following scientists contribute to our knowledge of the atom?

a. Crookes	c. Goldstein	e. Roentgen
b. J. J. Thomson	d. Millikan	f. Becquerel
- What evidence is there that electrons are particles?
- Why was Thomson's model of the atom discarded?
- Discuss Rutherford's gold foil experiment. What did it tell us about the structure of the atom?
- How many electrons, how many protons, and how many neutrons are there in a neutral atom of each of the following elements.

a. carbon (C)	c. aluminum (Al)	e. argon (Ar)
b. fluorine (F)	d. potassium (K)	f. sulfur (S)
- Consulting only the periodic chart, draw electron shell diagrams of each of the following elements.

a. lithium (Li)	c. silicon (Si)	e. calcium (Ca)
b. nitrogen (N)	d. chlorine (Cl)	f. phosphorus (P)
- What is the maximum number of electrons in the third energy level ($n = 3$)? In the fourth energy level ($n = 4$)?
- What is the difference between a Bohr orbit and the orbital of wave mechanics?
- What similarity in electronic structure is shared by lithium, sodium, and potassium? By beryllium, magnesium, and calcium?
- How many electrons are there in the outermost energy level of an atom of each of the following elements?

a. C	b. Ne	c. F	d. Al	e. Mg
------	-------	------	-------	-------
- Which of the following are metals and which are nonmetals? (The heavy line that looks like stair steps on the periodic chart divides the metals on the left from the nonmetals on the right.)

a. C	b. Fe	c. Na	d. Cl	e. Mg
------	-------	-------	-------	-------
- Which of the following elements are in the same group? Which are in the same period?

a. Mg	b. Al	c. Ca	d. Cl	e. Sr
-------	-------	-------	-------	-------
- Elements are defined on a theoretical basis as being composed of atoms that all have the same atomic number. On the basis of this theory, would you think it possible that someone might discover a new element that would fit between magnesium (atomic number = 12) and aluminum (atomic number = 13)?

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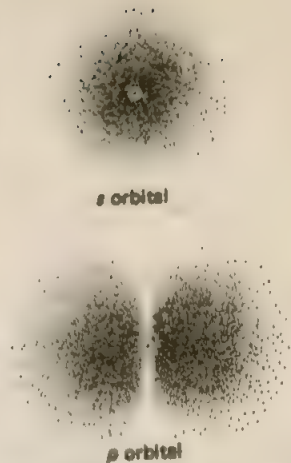


Figure 3.25 Charge cloud representations of atomic orbitals.

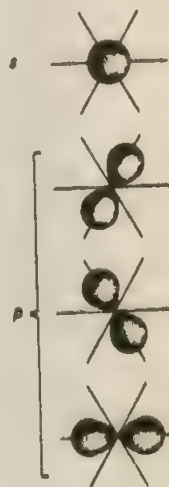


Figure 3.26 Outline representations of atomic orbitals. The three p orbitals differ only in their orientation in space.

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chapter 4

The Nucleus: Getting to the Heart of Matter

In chapter 3, we took a brief look at the atomic nucleus and then we turned our attention to electrons. For a major portion of this book, we take special note of the outermost electrons. It is the interaction of these particles that holds atoms together to make up the materials of the world. For the moment, however, let us turn to that tiny, tiny speck of matter called the *nucleus*.

Whole atoms are 10,000 times larger than atomic nuclei; yet, from the nucleus come radioactive particles and even the enormous power of nuclear bombs. In this chapter, we discuss radioactivity and some of its applications in medicine, agriculture, and archaeology. We also talk about nuclear bombs, fallout, and the effects of radiation on living things. The important topic of nuclear power plants is covered in a later chapter.

It seems that much of what we hear today about nuclear processes is negative, and we hear about bombs and about problems at nuclear power plants. But there is a positive side, too. Nuclear medicine saves lives. Diseases once regarded as incurable can be diagnosed and treated effectively with radioactive isotopes. Applications of nuclear chemistry to biology, industry, and agriculture have improved the human condition significantly. The use of radioisotopes in biological and agricultural research has led to increased crop production, which provides more food for a hungry world. Although the threat of annihilation from nuclear warfare still hangs over our heads like a dark cloud, it is far more likely that you will be saved by nuclear medicine than that you will be killed by a nuclear explosion.

A Partial Parts List for the Atomic Nucleus

We saw in chapter 3 that atomic nuclei are made up of protons and neutrons. Although nuclear physicists have extended this parts list to include at least a hundred particles, most of these particles have a transitory existence and are of little interest to a chemist. In this discussion, we take the oversimplified, but useful, view that atomic nuclei are made up of protons and neutrons—and some sort of force that holds them together.

Protons and neutrons have virtually the same mass—1.007276 and 1.008665 atomic mass units (amu) respectively. For many purposes, we can assume the mass is

the same—1 amu each. A proton has a charge equal in magnitude but opposite in sign to that of an electron. This charge on a proton is written as $1+$. The electron has a mass of 0.000549 amu—essentially 0 for many purposes—and a charge of $1-$. The parts list of subatomic particles is summarized in **table 4.1**.

The number of protons in the nucleus of an atom of any element is the atomic number of that element. This number determines the kind of atom, that is, the element. For example, an atom with 26 protons (an atom with an atomic number of 26) is an atom of iron (Fe). An atom with 92 protons is an atom of uranium (U). The number of neutrons in a given kind of nucleus can vary, however. Most hydrogen (H) atoms have a nucleus consisting of one proton and no neutrons. About 1 hydrogen atom in 5000, however, does have a neutron as well as a proton in the nucleus. Both kinds are hydrogen atoms. Atoms that have this sort of relationship—the same number of protons but different numbers of neutrons—are called *isotopes*.

Table 4.1
Subatomic particles

Particle	Symbol	Approximate Mass	Charge
Proton	p	1	$1+$
Neutron	n	1	0
Electron	e	0	$1-$

There is a quite rare third isotope of hydrogen (tritium), that has one proton (that's what makes it hydrogen) and two neutrons. **Figure 4.1** includes shell diagrams for the three isotopes of hydrogen. Most, but not all, elements exist in nature in isotopic forms. An interesting and easy to remember example is that of the element tin (Sn), which exists in 10 isotopic forms.

Isotopes are of little importance in ordinary chemical reactions. Both the light (ordinary) hydrogen atoms and the heavy hydrogen (deuterium) atoms react with oxygen to form water. Since deuterium atoms are about twice as heavy as ordinary hydrogen atoms, compounds formed with different hydrogen isotopes have different physical properties, but such differences are usually slight. In nuclear reactions, isotopes are of utmost importance, as we will see.

Nuclear Arithmetic

To represent the different isotopes, symbols with subscript and superscript numbers are used. In the general symbol



the Z represents the *atomic number*, that is, the number of protons. The A represents the *mass number*—the number of protons plus the number of neutrons. In the symbol



the number of protons is 17. The number of neutrons is $(35 - 17) = 18$.

The Z number is not necessary to identify the element—the symbol does that—but it is convenient for chemists to use in writing nuclear reactions.

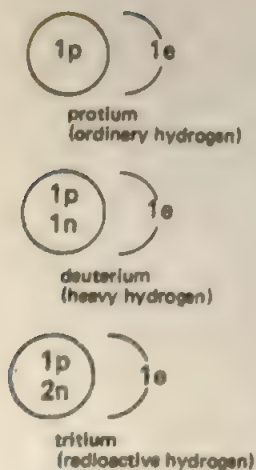


Figure 4.1 The isotopes of hydrogen. Deuterium and tritium are used in the hydrogen bomb (p. 66).

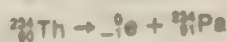
Natural Radioactivity

Some nuclei are unstable as they occur in nature. Radium atoms with a mass number of 226, for example, break down spontaneously, giving off alpha particles. Since alpha particles are identical with helium nuclei, this process can be summarized by the equation

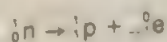


The new element, with two fewer protons, is identified by its atomic number (86) as radon (Rn).

Thorium nuclei also are unstable. The isotope with a mass number of 234 decomposes by beta decay. Since the beta particle is identical with an electron, this process can be written



The new element, with one more proton, is identified by its atomic number as protactinium (Pa). The gain of a proton and the emission of an electron can be interpreted as the change of a neutron in the nucleus into a proton plus an electron



The third type of radioactivity is called gamma decay. Since this type of emission involves no particle, no equation need be written. Gamma emission usually accompanies the emission of alpha or beta particles.

The major types of radioactive decay and the ensuing nuclear changes are summarized in table 4.2.

Half-life

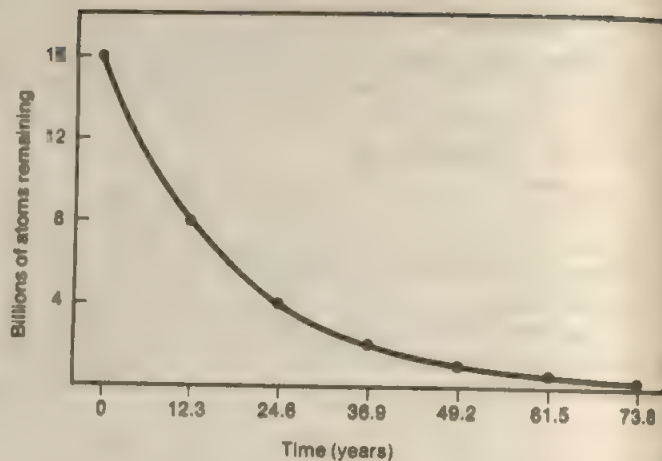
Thus far we have discussed radioactivity as applied to single atoms. In the laboratory, we generally deal with great numbers of atoms—numbers far larger than the number of people on all the earth. If we could see the nucleus of an individual atom, we could tell *whether* or not it would undergo radioactive decay by noting its composition. Certain combinations of protons and neutrons are unstable. We could not, however, determine *when* the atom would undergo a change. Radioactivity is a random process, generally independent of outside influences.

With large numbers of atoms, the process of radioactive decay becomes more predictable. A measurable quantity, called a *half-life*, is a characteristic property of each radioactive isotope. This half-life can be very long, as with uranium-238 (with a half-life of 4.5 billion years), or very short, as with boron-9 (with a half-life of 8×10^{-10} second).

Table 4.2
Radioactive decay and nuclear change

Type of Radiation	Symbol	Mass Number	Charge	Change in Mass Number	Change in Atomic Number
Alpha	α	4	2+	Decreases by 4	Decreases by 2
Beta	β	0	1-	No change	Increases by 1
Gamma	γ	0	0	No change	No change

Figure 4.2 The radioactive decay of ${}^3\text{H}$.



The half-life of a radioactive isotope is that period of time in which 50% of the original number of atoms undergo radioactive decay. Suppose, for example, that we had 16 billion atoms of the radioactive hydrogen isotope tritium. The half-life of this isotope is 12.3 years. This means that in 12.3 years 8 billion of the atoms would have undergone radioactive decay. In another 12.3 years, half the remaining atoms have decayed. That is, after two half-lives 25% of the original atoms would remain unchanged. Two half-lives do not make a whole! This concept of half-life is shown graphically in figure 4.2.

It is impossible to say exactly when *all* of the ${}^3\text{H}$ atoms would have decayed. For practical purposes* we can assume that nearly all the radioactivity would be gone after about 10 half-lives. For the tritium sample considered here, 10 half-lives would be 123 years.

Artificial Transmutation

The forms of radioactivity we have encountered so far occur in nature. Other nuclear reactions can be brought about by bombarding stable nuclei with alpha particles, neutrons, or other subatomic particles. These particles, given sufficient energy, penetrate the formerly stable nucleus and bring about some form of radioactive emission. This sort of nuclear change brings about a transmutation—one element is changed into another.

Ernest Rutherford, a few years after his famous gold foil experiment (chapter 3), studied the bombardment of a variety of light elements with alpha particles. One such experiment, in which he bombarded nitrogen, resulted in the production of protons.

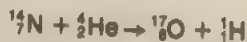


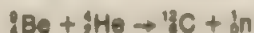
Figure 4.3. Frédéric and Irène Joliot-Curie discovered artificially induced radioactivity in 1934. (Reprinted with permission from Weeks, Mary E., *Discovery of the Elements*, Easton, Pa.: Chemical Education Publishing, 1968. Copyright © 1968 by the Chemical Education Publishing Company.)

*Half-life can be illustrated by a rather corny story. A boy is going to see his girl, who lives exactly 256 m away. He covers half the distance (128 m) in the first minute, half the remaining distance (64 m) in the second minute, half the remainder (32 m) in the third minute, and so on. Since he never goes more than half the remaining distance in any time interval, he never quite gets there. But, after 10 minutes, he is close enough (25 cm) for practical purposes.



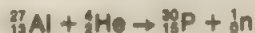
(Recall that the hydrogen nucleus is a proton; hence the alternative symbol ${}^1_1\text{H}$ for the proton.) Rutherford had postulated the existence of protons in nuclei in 1914. This experiment, published in 1919, gave the first experimental verification of the existence of these fundamental particles. It was also the first nuclear reaction initiated by a human.

A great many transmutations were carried out during the 1920s. In 1932, James Chadwick discovered the neutron by bombarding beryllium with alpha particles.



Induced Radioactivity

The first nuclear reactions initiated in a laboratory produced isotopes already known to occur in nature. This was perhaps fortuitous, for it was inevitable that an unstable nucleus would be produced sooner or later. Irène Curie (daughter of the 1903 Nobel Prize winners) and her husband Frédéric Joliot were studying the bombardment of aluminum with alpha particles. Neutrons were produced, leaving behind an isotope of phosphorus.



Much to their surprise, the target continued to emit particles after the bombardment was halted. The isotope of phosphorus was radioactive, emitting particles equal in mass to the electron but opposite in charge. These particles are called *positrons*. The reaction the scientists were observing is written



Irène and Frédéric won a Nobel Prize of their own in 1935.

Nuclear Sleuths

Scientists in a wide variety of fields make use of radioisotopes as tracers in physical, chemical, and biological systems. Isotopes of a given element, whether radioactive or not, behave nearly identically in chemical and physical processes. Since radioactive isotopes are easily detected, it is relatively easy to trace their movements, even through a complicated system.

As a simple example, let's consider the flow of a liquid through a pipe. Suppose there is a leak in a pipe buried beneath a concrete floor. We could locate the leak by digging up extensive areas of the floor. Or we could add a small amount of radioactive material to liquid going into the drain and trace the flow of liquid with a Geiger counter—an instrument that detects radioactivity. Once the leak had been located, only a small area of the floor would need to be dug up to repair the leak. Short-lived isotopes—which disappear soon after doing their job—usually are employed for such purposes.

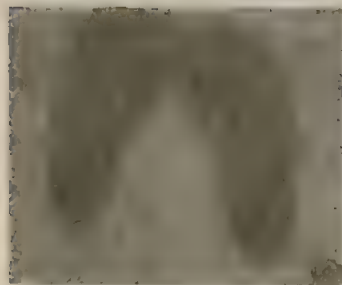
In a similar manner, we could trace the uptake of phosphorus by a green plant. The plant is fed some fertilizer containing radioactive phosphorus. A simple method of detection involves placing the plant on a photographic film. Radiation from the phosphorus isotopes exposes the film, much as light does. This type of exposure, called an *autoradiograph*, shows the distribution of phosphorus in the plant (figure 4.4).

Radioisotopes are widely used in medicine. For example, iodine-131 is used to determine the size, shape and activity of the thyroid gland. The body concentrates



Figure 4.4 Autoradiograph showing the uptake of phosphorus in a green plant (Courtesy of the United States Department of Energy.)

Figure 4.5 A linear photoscanner produced these pictures. (a) A normal thyroid. (b) An enlarged thyroid. (c) A cancerous thyroid. (Courtesy of the United States Department of Energy.)



iodine in this gland. Radioactive iodine behaves almost exactly as does ordinary iodine in the body, but it can be detected from outside the body. **Figure 4.5** shows pictures of the thyroid made by a device called a linear photo scanner.

Brain tumors tend to absorb certain ions. For this reason, arsenic-74 ($^{74}_{33}\text{As}$), in ionic form, can be used in the detection of these growths. Arsenic-74 is a positron ($^0_{+1}\text{e}$) emitter.



When a positron encounters an electron (in any ordinary matter there are numerous electrons), two gamma rays are produced.



These travel in exactly opposite directions. Detectors can be placed on opposite sides of a patient's head. When each detector simultaneously "sees" a gamma ray, a count is made. When the recorders are set so that two simultaneous gamma rays (both produced in the annihilation of the positron and electron) must be seen to be recorded, gamma rays resulting from natural background radiation are ignored. Thus, the tumor can be precisely located.

Several types of cancers concentrate phosphate ions to a much greater extent than does healthy tissue. Therefore, phosphate labeled with phosphorus-32 ($^{32}_{15}\text{P}$) can be used to detect these cancer cells. Since phosphorus-32 emits only beta particles, which have relatively low penetrating power, the detector must be placed very close to the suspect cells.



This limits the use of this method to diagnosis of skin cancer and cancer of tissue exposed by surgery.

Sodium-24 ($^{24}_{11}\text{Na}$) is used to detect constriction or obstruction in blood vessels. A little salt (sodium chloride) containing sodium-24 ions is injected into a vein in an arm or a leg. A counter is used to detect the arrival of the radioisotope in another part of the body. The time it takes to get there tells whether or not there are obstructions in the circulatory system.

For diagnostic scanning, we can imagine an ideal isotope. The isotope would be a gamma emitter. For scanning, we wish to detect radiation outside the body and therefore we desire a radiation that can escape from the body, that is, one that has good penetrating power. It would be best if neither alpha nor beta particles were emitted. These are not needed for detection and would simply do unnecessary damage to the body. The gamma rays should have just the right energy—not so weak that we would have to wait around forever to get enough of a response from our detector and not so strong that they would impart unnecessary energy to the body in making their way out. The half-life also should be just right—not so short that the activity is gone before we can measure it and not so long that significant activity remains long after we have finished our studies.

Happily there is available an isotope very much like this. It is technetium-99^m ($^{99}_{43}\text{Tc}^m$). The *m* stands for *metastable*, which means that this isotope will give up some energy to become a more stable version of the same isotope (one with the same atomic number and the same atomic weight). The energy it gives up is the gamma ray we need for detecting the isotope while scanning. The energy of the gamma ray is just about right, and so is the half-life, about 6 hours. With this short a half-life, we must

plan carefully our use of the isotope. In fact, the isotope itself is not what is purchased. The technetium-99^m is formed by the decay of molybdenum-99.



A container of this molybdenum isotope is obtained, and the decay product, technetium-99^m, is milked from the container as it is needed.

Much effort has gone into making technetium-99^m available in a variety of preparations. In some forms, it is useful for kidney scanning; in other forms, it is concentrated by the liver and spleen. It also can be used for brain scans and for lung scans. Thus, this isotope can replace a number of less than ideal radioisotopes.

Radioisotopes also are widely used to determine the mechanism of drug action. Drug molecules are tagged with radioactive atoms. These can be traced through the complex biochemical processes that occur when a drug is metabolized.

Table 4.3 is a list of some radioisotopes in common use in medicine. The list is necessarily incomplete.

Even this abbreviated discussion should give you an idea of the importance of radioisotopes in medicine. The claim that nuclear science has saved more lives than nuclear bombs have destroyed is not an idle one.

Radioactive tracers also are put to good use in agricultural research. They are used to study the effectiveness of fertilizers and weed killers, to compare the nutritional value of various feeds, and to determine the best methods for controlling insects. The purposeful mutation of plants by irradiation has produced new and improved strains of commercially valuable crop plants ranging from tobacco to peanuts.

Radioisotopes have been used extensively in basic scientific research. The mechanism of photosynthesis was worked out in large part by using carbon-14 (¹⁴C)

Table 4.3
Some medical applications of radioisotopes

<i>Isotope</i>	<i>Name</i>	<i>Use(s)</i>
⁷⁴ As	Arsenic-74	Location of brain tumors
⁵¹ Cr	Chromium-51	Determination of volume of red blood cells and total blood volume
⁵⁸ Co	Cobalt-58	Determination of uptake of vitamin B ₁₂
⁶⁰ Co	Cobalt-60	Radiation treatment of cancer
¹³¹ I	Iodine-131	Detection of thyroid malfunction; measurement of liver activity and fat metabolism; treatment of thyroid cancer
⁵⁹ Fe	Iron-59	Measurement of rate of formation and lifetime of red blood cells
³² P	Phosphorus-32	Detection of skin cancer or cancer of tissue exposed by surgery
²²⁶ Ra	Radium-226	Radiation therapy for cancer
²⁴ Na	Sodium-24	Detection of constrictions and obstructions in the circulatory system
⁹⁹ Tc ^m	Technetium-99 ^m	A number of diagnostic uses (see text)
³ H	Tritium	Determination of total body water

as a tracer. Metabolic pathways in plants, animals, and humans are being studied by radioactive tracers. The potential for the use of this knowledge for human good is as enormous as the potential for the use of nuclear bombs for evil.

The Dating Game

The half-lives of certain isotopes can be used to estimate the age of rocks and archaeological artifacts. Uranium-238 decays with a half-life of 4.5 billion years. The initial products of this decay are also radioactive, and breakdown continues until an isotope of lead (^{206}Pb) is formed. By measuring the relative amounts of uranium-238 and lead-206, chemists can estimate the age of a rock. Some of the older rocks on the earth have been found to be from 3.0 to 3.5 billion years old. Moon rocks and meteorites have been dated at a maximum age of about 4.5 billion years. Thus, the age of the earth is generally estimated to be 4.5 to 5.0 billion years.

The dating of artifacts usually involves a radioactive isotope of carbon. Carbon-14 is formed in the upper atmosphere by the bombardment of ordinary nitrogen by neutrons from cosmic rays.



This process leads to a steady-state concentration of carbon-14 on the earth. Living plants and animals incorporate this isotope as carbon dioxide. When they die, however, the incorporation of carbon-14 ceases, and the carbon-14 in the plants and organisms decays, with a half-life of 5730 years, to nitrogen-14 ($^{14}_7\text{N}$). Thus, we merely need to measure the $^{14}_6\text{C}$ activity remaining in an artifact of plant or animal origin to determine its age. For example, a sample that has *half* the $^{14}_6\text{C}$ activity of new plant material is 5730 years old; it has been dead for one half-life. Similarly, an artifact with 25% the $^{14}_6\text{C}$ activity of new plant material is 11,460 years old; it has been dead for two half-lives.

Carbon-14 dating, as outlined here, assumes that the formation of the isotope was constant over the years. Recent evidence has indicated that this is not quite the case. However, for the most recent 7000 years or so, carbon-14 dates have been correlated with those obtained from the annual growth rings of trees. Calibration curves have been constructed from which accurate dates can be determined. Generally, carbon-14 is reasonably accurate for dating objects up to about 50,000 years old. Objects older than that have too little of the isotope left for accurate measurement.

Charcoal from the fires of an ancient people, dated by determining the $^{14}_6\text{C}$ activity, is used to estimate the age of other artifacts found at the same archaeological site. Carbon-14 dating also has been used to detect forgeries of supposedly ancient artifacts. Dating procedures based on research in the structure and stability of atomic nuclei have become the routine yet vital tools of archaeology.

Tritium, the radioactive isotope of hydrogen (p. 44), also is useful for dating. Its half-life of 12.3 years makes it useful for dating items up to about 100 years old. An interesting application is the dating of brandies. The alcoholic beverages are quite expensive when aged from 10 to 50 years. Tritium dating can be used to check the veracity of advertising claims about the aging process of the most expensive kinds.

Many other isotopes are useful for estimating the ages of objects and materials. Several of the more important ones are listed in table 4.4.

Einstein's Equation

Let's return now to our study of the history of radioactivity. Perhaps the most noted development of our age was a theoretical one, worked out with a pencil and

Table 4.4
Several isotopes useful in radioactive dating

<i>Isotope</i>	<i>Half-life (in years)</i>	<i>Useful Range</i>	<i>Dating Applications</i>
Carbon-14	5730	500 to 50,000 years	Charcoal, organic material
Tritium (^3H)	12.3	1 to 100 years	Aged wines
Potassium-40	1.3×10^9	10,000 years to the oldest Earth samples	Rocks, the Earth's crust, the moon's crust
Rhenium-187	4.3×10^{10}	4×10^7 to the oldest samples in universe	Meteorites
Uranium-238	4.5×10^9	10^7 to the oldest Earth samples	Rocks, the Earth's crust

note pad. These are not the tools we usually think of when thinking of a scientist. Albert Einstein may well be the best-known scientist of all time, yet his achievements were those of the mind, not the laboratory.

By 1905, Einstein had worked out his special theory of relativity. In doing this, he derived a relationship between matter and energy. The now-famous equation is written

$$E = mc^2$$

where E represents energy, m represents mass, and c is the speed of light. According to Einstein, energy and mass are different aspects of the same thing. Conversion of a small amount of matter yields a tremendous quantity of energy. One gram of matter is equivalent to 9×10^{13} J (90 000 million British thermal units, Btu). That is enough energy to heat the average home for 1000 years.

Nuclear Power and Nazism

A group of physicists headed by the Italian Enrico Fermi was first to study the bombardment of uranium with neutrons, but they failed to interpret their work properly. The German chemists Otto Hahn and Fritz Strassman first correctly interpreted the experiments after discovering the much lighter elements barium (Ba), lanthanum (La), and cerium (Ce) in the reaction products. The uranium atom had been split! Lise Meitner and Otto Frisch calculated the energy associated with the fission of uranium and found it to be several times greater than that of any previously known nuclear reaction. In addition, the splitting resulted in the release of more neutrons. These could split other uranium atoms, producing enormous amounts of energy (figure 4.7).

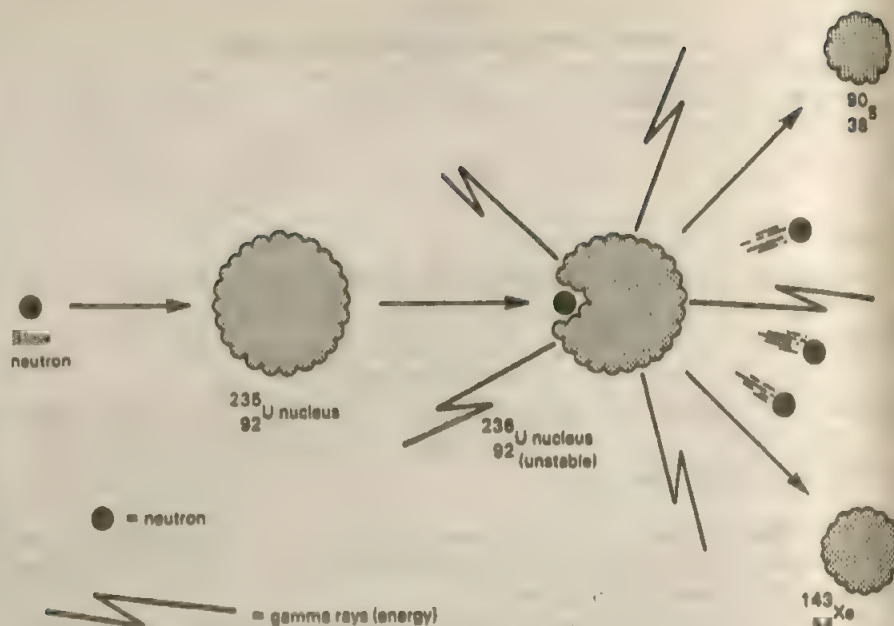
In 1938, Nazi Germany invaded and annexed Austria. Lise Meitner, an Austrian Jew, fled to Sweden. There she released the news of these momentous discoveries. This news was carried to the United States by Niels Bohr, the Danish physicist who is so well known for his quantum theory of the electronic structure of atoms. Fermi, who had fled Italy to the United States because his wife was Jewish, prevailed on the great Einstein to sign a letter to President Franklin D. Roosevelt to inform him of the importance of the discovery.

The United States government launched a massive research project for the study of atomic energy. Uranium had to be collected and the isotopes separated, for only



Figure 4.6 Albert Einstein. (Courtesy of Matheson Gas Products, East Rutherford, N.J.)

Figure 4.7 The splitting of a uranium atom. The neutrons produced in this fission can split other uranium atoms, thus sustaining a chain reaction. The splitting of one uranium-235 atom yields 8.9×10^{-16} kilowatt-hours (kwh) of energy. Fission of 235 g of uranium-235 (602×10^{23} atoms) produces 5 300 000 kwh of energy.



the relatively rare $^{235}_{92}\text{U}$ isotope is fissionable. The neutrons, it was found, had to be slowed by graphite to increase the probability of their hitting a uranium nucleus.

Fermi and his group achieved the first sustained nuclear reaction on 2 December 1942, under the bleachers at Stagg Field at the University of Chicago.

Separation of uranium-235 from the more abundant uranium-238 proceeded very slowly at a top-secret installation at Oak Ridge, Tennessee. This separation could not be done by chemical reaction, because the isotopes are identical chemically. Separation was accomplished by converting all the uranium to uranium hexafluoride, UF_6 . Molecules of UF_6 containing the $^{235}_{92}\text{U}$ isotope would be slightly lighter and hence would move slightly more rapidly than those molecules containing the $^{238}_{92}\text{U}$ isotope. By allowing the gaseous UF_6 to diffuse through thousands of consecutive pinholes, the scientists eventually obtained 15 kg of uranium-235, enough to make a small explosive device.

While the tedious work of separating uranium isotopes was under way at Oak Ridge, other workers, led by Glenn T. Seaborg, had discovered that uranium-238 could be converted into new elements by bombardment with neutrons. The new elements were named neptunium (Np) and plutonium (Pu). One isotope of plutonium, $^{239}_{94}\text{Pu}$, was found to be fissionable and thus suitable material for use in a bomb. A series of large reactors was built near Hanford, Washington, for the manufacture of plutonium.

Before a fissionable material can sustain a chain reaction, a certain minimum amount of fissionable material, called the *critical mass*, must be brought together. There must be enough fissionable nuclei that the neutrons released in one fission process would have a good chance of finding another fissionable nucleus before escaping from the mass.

By July 1945, enough plutonium had been made to assemble a bomb. This first A-bomb was tested in the desert near Alamogordo, New Mexico, on 16 July 1945. The heat from the explosion vaporized the 30-m steel tower on which it had been placed and melted the sand for several acres around the site. The light released was the brightest a human had ever seen.



Figure 4.8 Enrico Fermi. (Courtesy of Mrs. Laura Fermi.)



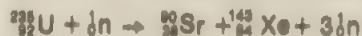
Figure 4.9 A nuclear bomb of the type exploded over Hiroshima. The bomb is 71 cm in diameter and 305 cm long; it weighs 4000 kg and has an explosive power equivalent to about 18 000 000 kg of high explosive. (Courtesy of the National Air and Space Museum, Smithsonian Institution, Washington, D.C.)

Some of the scientists were so awed by the force of the blast that they argued against using it against Japan. Some, led by Leo Szilard, argued for a demonstration of its power at an uninhibited site. But fear of a well-publicized dud and the desire to avoid millions of casualties in an invasion of Japan led President Harry S. Truman to order the dropping of the bombs on Japanese cities. A uranium bomb called "Little Boy" was dropped on Hiroshima on 6 August 1945, causing over 100,000 casualties (figures 4.9 and 4.10). Three days later, a plutonium bomb called "Fat Man" was dropped on Nagasaki with comparable results. World War II ended with the surrender of Japan on 14 August 1945.

Fallout

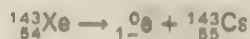
When an atomic bomb explodes, it produces a fantastic amount of heat, devastating shock waves, and deadly gamma radiation. Even then it is not through, for the products of uranium fission are radioactive. These can rain upon the Earth, even thousands of miles away, days and weeks later.

A typical fission reaction might be:



The neutrons may strike additional uranium atoms, carrying on the chain reaction. The strontium (Sr) and xenon (Xe) atoms are radioactive and are a part of the fallout.

The uranium atom can split in 40 or more ways, producing 80 or 90 primary radioactive products. Some of these produce radioactive *daughter* isotopes. For example, xenon-143 (${}^{143}_{54}\text{Xe}$) undergoes beta decay, with a half-life of 1 second.



The cesium isotope is also radioactive—as are its daughters and their daughters. Still other radioisotopes, such as carbon-14 and tritium, are formed by the impact of neutrons produced in the explosion on molecules of the atmosphere. Thus, fallout is exceedingly complex. We can consider only a few of the more important isotopes in this discussion.

Of all the isotopes, strontium-90 (${}^{90}_{38}\text{Sr}$) presents the greatest hazard to people. This isotope has a half-life of 28 years. Strontium-90 reaches us primarily through



Figure 4.10 The now familiar mushroom cloud that follows an atomic explosion. This photograph was taken just after the first atomic bomb destroyed Hiroshima. (Courtesy of the National Air and Space Museum, Smithsonian Institution, Washington, D.C.)

our consumption of milk and vegetables (figure 4.11). Because of its similarity to calcium (both are Group IIA elements), strontium-90 is incorporated into bone. There it remains a source of internal radiation for many years.

Although strontium-90 is a greater long-term hazard, iodine-131 ($^{131}_{53}\text{I}$) may present a greater threat immediately after a nuclear explosion. The half-life of iodine-131 is only 8 days, but it is produced in relatively large amounts. Iodine-131 is efficiently carried through the food chain (figure 4.12). In the body it is concentrated in a small area, the thyroid gland. It is precisely this characteristic that makes this same isotope so useful for diagnostic scanning. However, for a healthy individual, the incorporation of radioactive iodine into the thyroid gland offers only damaging side effects.

Figure 4.11 Pathways of strontium-90 from fallout. (Reprinted from Comer, C. L., *Fallout*, Oak Ridge, Tenn.: United States Energy Research and Development Administration, 1966.)

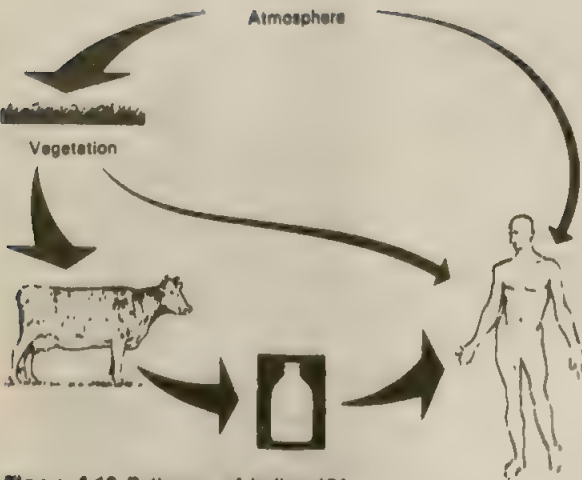
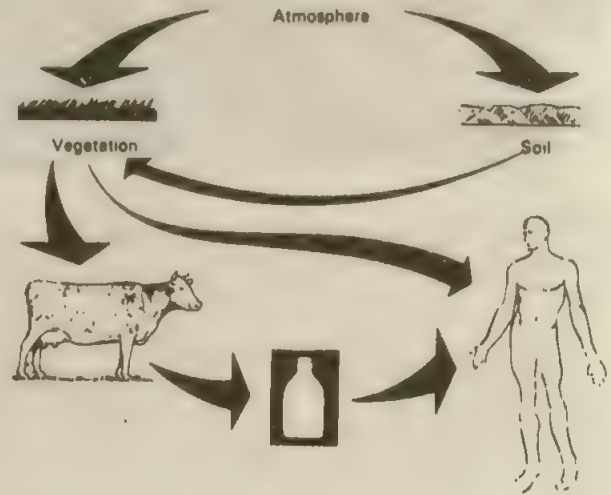


Figure 4.12 Pathways of iodine-131 from fallout. (Reprinted from Comer, C. L., *Fallout*, Oak Ridge, Tenn.: United States Energy Research and Development Administration, 1966.)

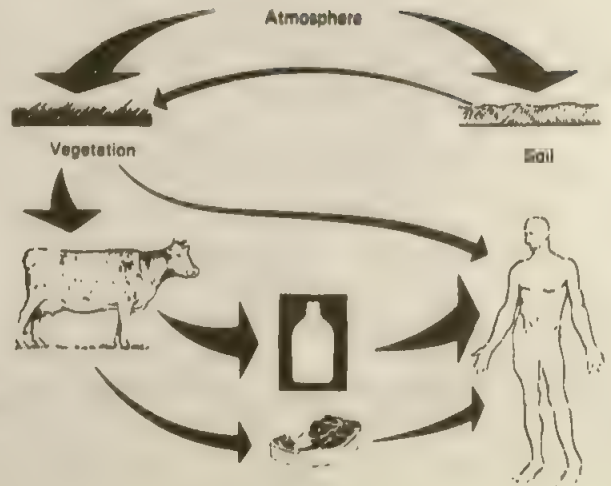


Figure 4.13 Pathways of cesium-137 from fallout. (Reprinted from Comer, C. L., *Fallout*, Oak Ridge, Tenn.: United States Energy Research and Development Administration, 1966.)

Another important isotope in fallout is cesium-137 (^{137}Cs). Cesium is similar to potassium (both are Group 1A elements), and it mimics potassium in the body. Cesium-137 is a gamma emitter and has a half-life of 30 years. It is less of a threat than strontium-90, though, because it is removed from the body more readily. We consume cesium-137 along with the vegetables, milk, and meat we eat (figure 4.13).

By the late 1950s, radioactive isotopes from atmospheric testing of nuclear weapons had been detected in the environment. Concern over radiation damage from nuclear fallout led to a movement to ban atmospheric testing. Many scientists were leaders in the movement. Linus Pauling, who won the Nobel Prize in chemistry in 1954 for his work in determining the structure of proteins, was a particularly articulate advocate of banning the bomb. In 1963, a nuclear test ban treaty was signed by the major powers—with the exception of France and the People's Republic of China, who continue above-ground tests. Since the signing of the treaty, India has joined the nuclear club by exploding a bomb above ground. Pauling, who had to endure being called a communist and a traitor for his outspoken position, was awarded the Nobel Prize for peace in 1962.

Radiation and Us

Soon after the discovery of X rays and radioactivity, it was noted that such radiation could be both beneficial and harmful. We are all familiar with the use of X rays in medical diagnosis. We have seen how radioisotopes are used in beneficial ways. But radiation also presents a hazard to living things. High-energy particles and rays knock electrons from atoms, forming ions. Such chemical changes, when they occur in living cells, can be highly disruptive. Water in the cells can be transformed to highly reactive hydrogen peroxide (H_2O_2), which can disrupt the delicate chemical balance in the cells. Particularly vulnerable are the white blood cells, the body's first line of defense against bacterial infection. Radiation also affects bone marrow, causing a drop in the production of red blood cells, which results in anemia. Radiation also has been shown to induce leukemia, a cancerlike disease of the blood-forming organs.

Radiation also causes changes in the molecules of heredity (DNA) in reproductive cells. Such changes show up as *mutations* in the offspring of exposed parents. Little is known of the effects of such exposure on humans. However, most of the mutations during the evolution of present species may have been caused by radiation from ever-present cosmic rays and from natural radioactivity in air, water, soil, and rocks.

Opponents of nuclear power plants worry about the effects of the increased radiation levels these plants bring. In 1979, an accident at the Three Mile Island plant near Harrisburg, Pennsylvania, released small amounts of radioactivity into the environment. This mishap did much to increase public concern about the safety of nuclear power plants. We discuss nuclear power, with its promise and peril, in chapter 13.

Binding Energy

Nuclear reactions involve tremendous energy changes. Where does all this energy come from? When neutrons and protons are put together to form nuclei, some mass is converted to energy. This is sometimes called *binding energy*. For example, if two protons and two neutrons were put together to form a helium nucleus, it should have a mass of

2 protons:	2×1.007276	$= 2.014552$	amu
2 neutrons:	2×1.008665	$= 2.017330$	amu
	total mass	$= 4.031882$	amu



Figure 4.14 Linus Pauling.

The actual mass of the helium nucleus is 4.001506 amu. The missing mass, or binding energy, is 0.030376 amu. Remembering Einstein's $E = mc^2$, we see that this small amount of mass is equivalent to a large amount of energy. If we made calculations like this for all nuclei and plotted the data on a graph, a curve like the one in **figure 4.15** would result. The most stable nuclei are those in the vicinity of iron (atomic number 26). Splitting uranium atoms produces daughter nuclei that are more stable than the original uranium atoms; consequently, this splitting releases considerable energy.

We also can see from the graph that we could produce even more energy by combining small nuclei (such as hydrogen) to form larger, more stable nuclei. This sort of nuclear fusion occurs in the explosion of a hydrogen bomb.

Thermonuclear Reactions

The source of nearly all our energy on Earth is the thermonuclear reactions taking place in the sun. The intense temperature in the center of the sun causes nuclei to fuse and release tremendous amounts of energy. The principal net reaction is believed to be the fusion of four hydrogen nuclei to produce one helium nucleus.



One gram of hydrogen, upon fusing, releases an amount of energy equivalent to 17 000 kg (nearly 20 tons) of coal.

The hydrogen bomb makes use of a uranium or plutonium (fission) bomb to provide the tremendous heat necessary to start the nuclei fusing. The fusion of ordinary hydrogen (^1_1H) occurs much too slowly, so the heavier isotopes deuterium (^2_1H) and tritium (^3_1H) are employed. The intense heat of the fission explosion starts the fusion of hydrogen nuclei.

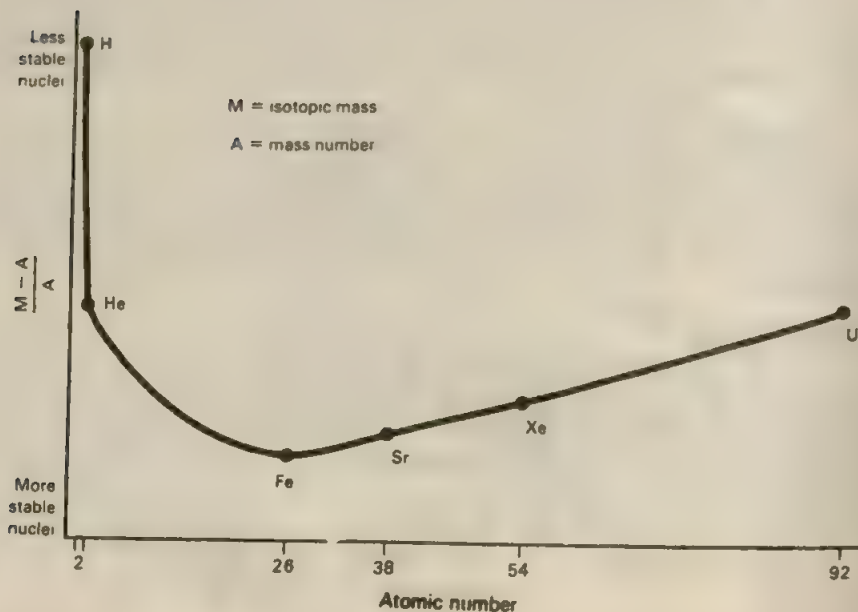
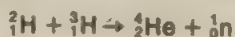


Figure 4.15 Nuclear stability.

The neutron released splits lithium atoms, forming more tritium



To date, the fusion reactions are useful only for making bombs. Research is progressing in the control of nuclear fusion. The prospect for power from controlled fusion is discussed in chapter 13.

The Nuclear Age

We live in an age during which fantastic forces have been unleashed. The threat of nuclear war has been a constant specter for the last three decades. Nuclear bombs have been used to destroy cities—and men, women, and children. Science and scientists have been deeply involved in it all.

Still, I cannot believe that the world would be a better place had we not discovered the secrets of the atomic nucleus. For one thing, more lives have been saved through nuclear medicine than have been destroyed by nuclear bombs. And no nuclear bombs have been used in warfare since 1945. Perhaps the terror of nuclear holocaust has done more than anything else to prevent World War III.

Problems

- Define each of the following terms.
 - isotope
 - deuterium
 - alpha particle
 - beta particle
 - gamma ray
 - half-life
 - fission
 - fusion
 - radioisotope
 - binding energy
 - artificial radioactivity
- Discuss the impact of nuclear science on the following topics. (See the list of references and readings for this chapter for resource materials.)
 - war and peace
 - industrial progress
 - medicine
 - agriculture
 - human, animal, and plant genetics
- A radioisotope decays to give an alpha particle and bismuth-211 (${}^{211}_{83}\text{Bi}$). What was the original element?
- How many protons and how many neutrons are there in each of the following nuclei?
 - ${}^{206}_{82}\text{Pb}$
 - ${}^3_1\text{H}$
 - ${}^{60}_{27}\text{Co}$
 - ${}^{233}_{90}\text{Th}$
- When magnesium-24 (${}^{24}_{12}\text{Mg}$) is bombarded with neutrons, protons are ejected. What new element is formed? (Hint: Write a balanced nuclear reaction.)
- Compare nuclear fission and nuclear fusion. Why is energy liberated in each case?
- C. E. Bemis and colleagues at Oak Ridge National Laboratory recently confirmed the identification of element 104, an artificial atom with a half-life of only 4.5 seconds. Only 3000 atoms of the element were created in the tests. How many atoms were left after 4.5 seconds? After 9.0 seconds? After 13.5 seconds?
- Plutonium is especially hazardous when inhaled or ingested because it emits alpha particles (${}^4_2\text{He}$). What new element is formed? (Write a balanced nuclear reaction.) Why would alpha particles cause more damage to tissue than beta particles (${}^0_{-1}\text{e}$)?
- Uranium-239 (${}^{239}_{92}\text{U}$) undergoes beta decay. Write a balanced nuclear equation for this process.
- Did President Harry S. Truman make the right decision when he decided to drop the nuclear bombs on Japanese cities? Would your answer be the same if you were living in 1945 and had relatives among the troops preparing for the invasion of Japan? If you were an inhabitant of one of the cities?
- The ratio of carbon-14 to carbon-12 in a piece of charcoal from an archaeological excavation is found to be 50% of that in a sample of modern wood. Approximately how

- old is the site? How old would it be if the ratio were 25% of that in a sample of modern wood?
12. How old is a bottle of wine if the tritium activity is 25% that of new wine?

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United States Department of Energy
Technical Information
P.O. Box 62
Oak Ridge, Tennessee 37830
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chapter 5

Chemical Bonds: The Ties That Bind

What are chemical bonds that you should be mindful of them? Bonds are the forces that hold atoms and ions together to form molecules and crystals. The type of bonding within molecules also determines the forces between molecules. The state of matter—whether it is solid, liquid, or gas—depends on bonding forces. Bonds even determine the physical shapes of molecules, that is, whether they are spherical or flat, rigid or wobbly. Bonding is of great interest to chemists, but what significance can it have for you? Perhaps a few examples will demonstrate the importance of chemical bonding.

Carbon has the unique ability to form huge molecules through repeated bonding of carbon atom to carbon atom to form long chain and ring structures. Such molecules are used to build carbohydrates, fats, and proteins, the components of foods—and of people.

The bonds of ozone molecules make life on earth possible. Ozone molecules break apart when they are struck by sunlight. Their sacrifice keeps the sun's ultraviolet rays from burning us all to a crisp.

The bonds of certain chemicals store the energy we need for breathing and for maintaining our heartbeats.

Because carbon monoxide bonds to the hemoglobin in our blood more tightly than does oxygen, carbon monoxide can kill us.

The action of some drugs depends on the shape (determined by bonding) of their molecules. Knowledge of molecular structure has enabled chemists to design not only drugs but also synthetic fabrics, plastics, insecticides, and thousands of other compounds with specific properties.

Here is one last example of the importance of bonding to life. The DNA molecule—the chemical basis of heredity—carries its genetic message in its bonds. Whether an organism is fish, fowl, hippopotamus, or human is determined by the bonding in the organism's DNA molecules. The color of your hair and eyes and your general body shape and size are determined by your inheritance of DNA. If you like your appearance, be grateful for chemical bonding. If you're less than thrilled with the color of your hair or the shape of your nose, consider this: our knowledge of chemical bonding may someday permit us to custom tailor genes, that is, to control

to some extent the structure of living matter. That's reason enough to be mindful of chemical bonds.

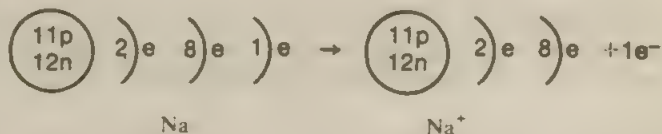
The Delightful Art of Deduction

In our discussion of the atom and its structure (chapters 2 and 3), we followed the historical development of some of the more important atomic concepts. Some of the nuclear concepts (chapter 4) were approached in the same manner. We could continue to look at chemistry in this manner, but that would require several volumes of print—if we got very far—and perhaps more of your time than you would care to spend. We won't abandon the historical approach entirely, but we will emphasize that other aspect of scientific enterprise: deduction.

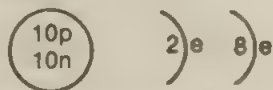
The art of deduction works something like this.

<i>Fact</i>	<i>Theory</i>	<i>Deduction</i>
The noble gases, such as helium, neon, and argon, are inert (i.e., they undergo few, if any, chemical reactions).	The inertness of the noble gases is due to their electronic structures (each has a filled outermost energy level).	If other elements could alter their electronic structures to become more like noble gases, they would become less reactive.

To illustrate, let's look at an atom of the element sodium (Na). It has 11 electrons, 2 in the first energy level, 8 in the second, and 1 in the third. If the atom could get rid of an electron, it would have the same electronic structure as an atom of the inert gas neon (Ne).

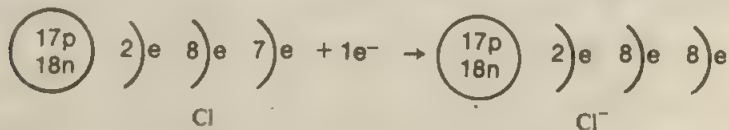


Recall that neon has the structure

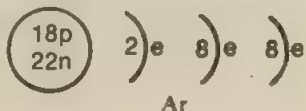


Let's immediately emphasize that the sodium ion (Na^+) and the neon atom (Ne) are not identical. The electron arrangement is the same, but the nuclei—and resulting charges—are not. As long as sodium keeps its 11 protons, it is still a form of sodium. But it is sodium *ion*, not sodium *atom*.

If a chlorine atom (Cl) could gain an electron, it would have the same structure as argon (Ar).

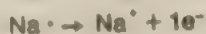


The structure of the argon atom is



The sodium, having lost an electron, becomes positively charged. It has 11 protons (11+) and only 10 electrons (10-). It is written Na^+ and is called a *sodium ion*. The chlorine atom, having gained an electron, becomes negatively charged. It has 17 protons (17+) and 18 electrons (18-). It is written Cl^- and is called a *chloride ion*. Note that a positive charge, as in Na^+ , indicates that one electron has been lost. Similarly, a negative charge, as in Cl^- , indicates that 1 electron has been gained.

In forming ions, the nuclei of sodium and chlorine and the *inner shells* (i.e., lower energy levels) of electrons do not change. Therefore, it is convenient to let the nucleus and the inner shells be represented by the *symbol alone*. Electrons in the outer, or *valence*, shell are represented by dots. Thus the shell diagrams for the ionization of sodium and chlorine are reduced to:



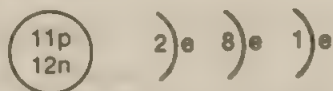
and



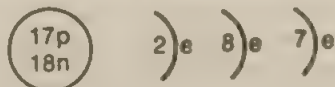
Representations of this sort are called *electron dot symbols*.

Mystery and Symbolism

The mystery of chemistry, to the nonchemist, is probably due in large part to chemists' use of symbolism. Chemists find it *convenient* to represent the sodium atom as $\text{Na} \cdot$ rather than the more complex



and, therefore, they do just that. And it is easier to write $:\ddot{\text{Cl}} \cdot$ than



so chemists often use the shorter form.

In practice, it is very easy to write electron dot formulas for elements in the first three periods (horizontal rows) of the periodic chart. The number of electrons in the outer shell is merely equal to the *group number*. Aluminum (Al) is in Group IIIA; therefore, it has three outer electrons. Sulfur (S) is in Group VIA; thus, it has six outer electrons. This generalization works fairly well for elements in A subgroups even beyond the first three periods. Thus, iodine (I) is in Group VIIA and has seven outer electrons, even though it is in the fifth period. **Table 5.1** gives the electron dot formulas for the first 20 elements.

Table 5.1
Electron dot symbols for the first 20 elements

IA	IIA	IIIA	IVA	VA	VIA	VIIA	Noble Gases
H \cdot							He:
Li \cdot	$\cdot\text{Be}\cdot$	$\cdot\ddot{\text{B}}\cdot$	$\cdot\ddot{\text{C}}\cdot$	$:\ddot{\text{N}}\cdot$	$:\ddot{\text{O}}\cdot$	$:\ddot{\text{F}}\cdot$	$:\ddot{\text{Ne}}:$
Na \cdot	$\cdot\text{Mg}\cdot$	$\cdot\ddot{\text{Al}}\cdot$	$\cdot\ddot{\text{Si}}\cdot$	$:\ddot{\text{P}}\cdot$	$:\ddot{\text{S}}\cdot$	$:\ddot{\text{Cl}}\cdot$	$:\ddot{\text{Ar}}:$
K \cdot	$\cdot\text{Ca}\cdot$						

Symbolism is a convenient, shorthand way of conveying a lot of information in a compact form. It is a chemist's most efficient and economical form of communication. Learning this symbolism is a good deal like learning a foreign language. Once you have learned a basic "vocabulary," the rest is a lot easier.

If Sodium and Chlorine Get Together—

Part I: Fact

Sodium is a highly reactive metal. It is soft enough to be cut with a knife. When freshly cut, it is bright and silvery, but it dulls rapidly by reacting with oxygen in the air. In fact, it reacts so readily in air that it is usually stored under oil or kerosene. Sodium reacts violently with water also, getting so hot that it melts. A small piece will form a spherical bead after melting and race around on the surface of the water as it reacts.

Chlorine is a greenish yellow gas. It is familiar as a disinfectant for swimming pools* and city water supplies. (The actual substance added may be a compound that reacts with water to form chlorine.) Who hasn't been swimming in a pool that had "so much chlorine in it that you could taste it"? Chlorine is extremely irritating to the respiratory tract. In fact, chlorine was used as a poison gas in World War I.

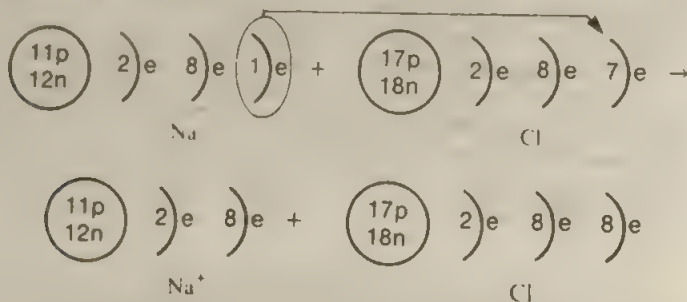
If a piece of sodium is dropped into a flask containing chlorine gas, a violent reaction ensues. A white solid that is quite unreactive is formed. It is a familiar compound—sodium chloride (table salt).

* Bromine, an element in the same family as chlorine, is now used as a disinfectant in some swimming pools.

If Sodium and Chlorine Get Together—

Part II: Theory

A sodium atom becomes less reactive by *losing* an electron. A chlorine atom becomes less reactive by *gaining* an electron. What happens when sodium atoms come into contact with chlorine atoms?* The obvious: chlorine extracts an electron from a sodium atom.



In the abbreviated electron dot form, this reaction is written



* Actually, the greenish yellow gas is composed of chlorine *molecules*, with each molecule consisting of two atoms. More about that later.

The sodium *ion*, Na^+ , and the chloride *ion*, Cl^- , not only have electronic structures like the inert gases (neon and argon, respectively) but they have opposite charges. Everyone knows that opposites attract. And, though this rule of thumb may not always work when applied to people, it works quite well for electrically charged particles. Remember that in even a minute amount of salt there are billions and billions of particles. These arrange themselves in an orderly fashion (**figure 5.1**). The arrangements are repeated in all directions—above and below, to the left and the right, toward the top and the bottom—to make up a *crystal* of sodium chloride. Each sodium ion attracts (and is attracted by) six chloride ions. Each chloride ion attracts (and is attracted by) the surrounding six sodium ions. The forces holding the crystal together are called *ionic bonds*.

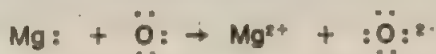
Models Revisited. Scientists sometimes use different models to represent the same system. The model employed in **figure 5.1** is a space-filling model showing the relative sizes of the sodium and chloride ions. Sometimes a ball-and-stick model is employed to better show the geometry of the crystal (**figure 5.2**.) From this model it is easy to see the cubic arrangement of the ions. You can also see that for each sodium ion there is one chloride ion; thus the ratio of ions is 1:1 and the simplest *formula* is NaCl . The symbols NaCl , written together, denote the *compound* sodium chloride. The formula also is used to represent one sodium ion and one chloride ion.

More Facts and a Generalization

Potassium (K), a metal similar to sodium, reacts with bromine (Br), a reddish brown liquid that is chemically similar to chlorine, to form a stable white crystalline solid (called potassium bromide).



Magnesium (Mg), a metal harder and less reactive than sodium, reacts with oxygen (O), a colorless gas, to form another stable white crystalline solid (magnesium oxide).



(Oxygen and bromine, like chlorine, are made up of diatomic *molecules*. The correct *equation* representing the reaction between potassium and bromine would be



The coefficient (for example, the 2 before the symbols) merely indicates the number of each atom or ion required. When no number appears before the symbol, a coefficient of 1 is understood.

Generally speaking, those elements on the left side of the periodic chart (especially those on the far left) react with those elements on the far right (excluding the noble gases) to form stable crystalline solids. The theory is that the elements on the left (metals) give up electrons to the elements on the right (nonmetals). The crystalline solids formed are held together by the attraction among oppositely charged ions—ionic bonds.

Covalent Bonds: A Share-the-Wealth Plan for Electron-Deficient Atoms

You might expect a hydrogen atom, with its one electron, to tend to acquire an

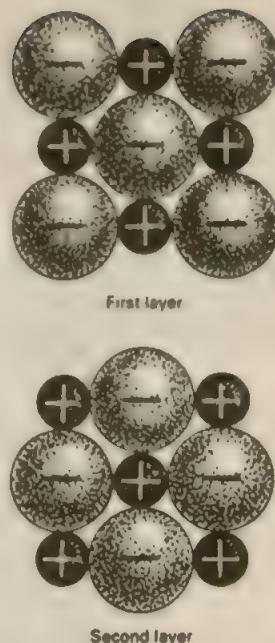


Figure 5.1 The arrangement of ions in a sodium chloride crystal.

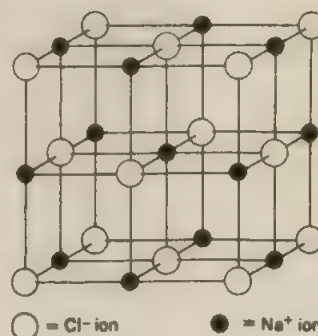
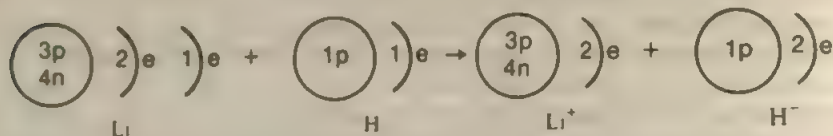


Figure 5.2 Ball-and-stick model of a sodium chloride crystal.

electron and assume the helium structure. Indeed, hydrogen atoms do just that in the presence of atoms of a reactive metal such as lithium.



Or, using electron dot formulas:



The :H⁻ is called a *hydride ion*. The compound formed, often simply represented by the formula LiH, is called lithium hydride. This compound sometimes is used to store hydrogen in the solid state. It reacts readily with water to form hydrogen gas.



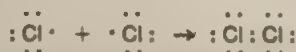
Only 8 g will produce over 20 L of hydrogen gas at ordinary temperatures and pressures.

But what if there are no other kinds of atoms around? What if there are only hydrogen atoms? One atom can't gain an electron from another, for among hydrogen atoms all have an equal attraction for electrons. They can compromise, however, by *sharing* a pair of electrons.



Both electrons occupy one orbital that encompasses both nuclei, with the two electrons spending most of their time somewhere between the two nuclei. The electron dot representation usually used, H:H, is, therefore, a fairly accurate representation. This combination of hydrogen atoms is called a *hydrogen molecule*. The bond formed by a shared pair of electrons is called a *covalent bond* or, because the pair of electrons is shared equally by the two atoms, a *nonpolar covalent bond*.

Chlorine atoms also can attain a more stable arrangement by sharing a pair of electrons:



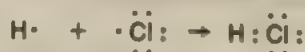
Here again the shared pair of electrons is called a covalent bond.

For simplicity, the hydrogen molecule often is represented as H₂ and the chlorine molecule as Cl₂. The subscripts indicate two atoms *per molecule*. In each case, the covalent bond between the atoms is understood.

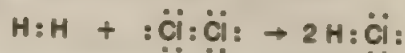
Some Atoms Are More Equal Than Others

So far we have seen that atoms combine in two ways. Atoms that are quite different in electronic structure react by the complete transfer of an electron from one atom to another (ionic bond formation). Atoms that are identical combine by sharing a pair of electrons (covalent bond formation). Now, let's look at some "in-betweeners."

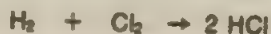
Hydrogen and chlorine react to form a colorless gas called hydrogen chloride. This reaction can be represented schematically by



Since both hydrogen and chlorine actually consist of diatomic molecules, the reaction is more accurately represented by the equation



For the sake of convenience and simplicity, this equation often is reduced to



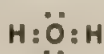
Molecules of hydrogen chloride consist of one atom of hydrogen and one atom of chlorine. These dissimilar atoms share a pair of electrons. Sharing does not mean sharing equally, however. Chlorine atoms have a greater attraction for shared electrons than hydrogen atoms do. Thus, the shared electrons spend more time in the bonding orbital of chlorine than in the bonding orbital of hydrogen. Since the electrons are more often found in the vicinity of the chlorine nucleus, that end of the molecule is more negative than the other. Thus, the hydrogen end is slightly positive. Such a covalent bond, in which the electron sharing is not equal, is called a *polar covalent bond*, or simply a *polar bond* (figure 5.3).

The gas hydrogen chloride dissolves readily in water. The aqueous solution formed is called hydrochloric acid (sometimes muriatic acid). This acid* is used for, among other things, cleaning toilet bowls and removing excess mortar from new brick buildings.

*Compounds called *acids* make up an important class of chemical substances. They—and a complementary family called *bases*—are discussed in some detail in chapter 7.

Water: A Crooked Molecule

Water is one of the most familiar chemical substances. The electrolysis experiment of Nicholson and Carlisle (chapter 2) and ample evidence gathered since their time indicate that the molecular formula for water is H_2O . On the basis of electronic structure, we would surmise that oxygen, with six electrons in its valence shell, would share electrons with each of two hydrogen atoms.



This arrangement completes the valence shell of oxygen, which then has the neon structure. It also completes the outer shell of each hydrogen atom (helium structure).

This linear representation for the water molecule is adequate for explaining some of the properties of water, but there are other phenomena that can only be explained by a bent arrangement of the atoms. For example, when placed between two charged plates, water molecules align themselves as *dipoles* (figure 5.4). It is evident that hydrogen-oxygen bonds ought to be polar, for hydrogen and oxygen would not be expected to share a pair of electrons equally. However, if the atoms were arranged in a straight line (i.e., in a linear arrangement), the two polar bonds would cancel one another and there would be no net dipole moment. Therefore, the atoms must be arranged at an angle. Precise (but indirect) measurements with sophisticated instruments show that the bond angle is 104.5° . Thus the charge distribution is

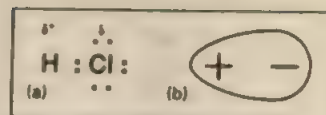
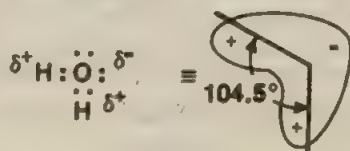


Figure 5.3 Representation of the polar hydrogen chloride molecule. (a) The electron dot formula, with the shared electron pair shown nearer chlorine. The symbols δ^+ and δ^- indicate partial positive and negative charges, respectively. (b) A diagram showing the hydrogen chloride molecule.

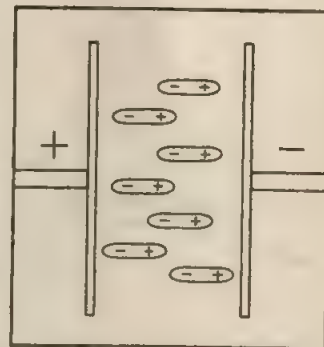


Figure 5.4 Molecules aligned as dipoles between charged plates. Dipoles are molecules with separate centers of positive and negative charge such that one end of the molecule appears positive and the other, negative.

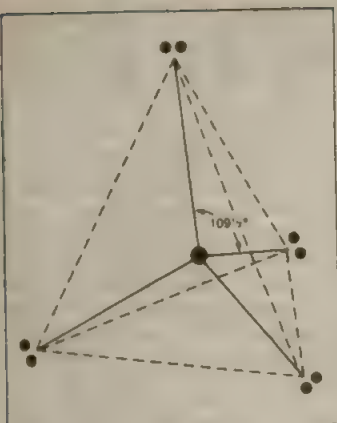


Figure 5.5 The four electron pairs around a central atom point toward the corners of a regular tetrahedron. Each angle is 109.5° .

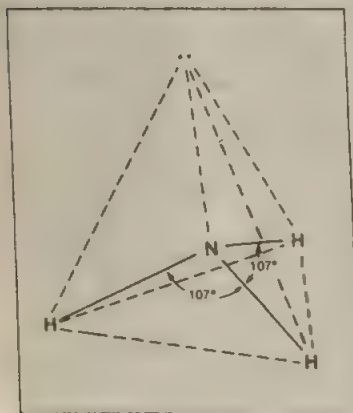


Figure 5.6 The pyramidal ammonia molecule.

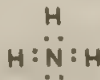
There are several theories of chemical bonding that can be used to account for the shape of the water molecule. One of the simplest and most satisfying is the valence shell electron pair repulsion (VSEPR) theory. There are four pairs of electrons in the outer (valence) shell of the oxygen atom in the water molecule. Since all electrons bear a like (negative) charge, it is reasonable to expect them to get as far apart as possible. If each pair of electrons is represented as a line extending out from the oxygen atom, the farthest apart these lines can get is 109.5° . Further, if the ends of these lines were all connected, the connecting line would inscribe a regular tetrahedron (**figure 5.5**).

The predicted tetrahedral angle of 109.5° is not far off the actual value of 104.5° for water. The disagreement is explained by the fact that only two of the electron pairs in water are shared with hydrogen atoms. The others, called *nonbonding pairs*, occupy a greater volume than do the bonding pairs, thus pushing the latter a little closer together.

We take a further look at the unique properties of water in chapter 9.

Ammonia: An Unshared Pair on a Tripod

An atom of the element nitrogen (N) has five electrons in its valence shell. It can assume the neon configuration by sharing pairs of electrons with *three* hydrogen atoms, thereby forming a molecule of ammonia.

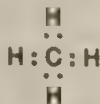


There are four pairs of electrons on the central nitrogen atom in the ammonia molecule. Using the electron pair repulsion theory, we would expect a tetrahedral arrangement of the four pairs and bond angles of 109.5° . The actual bond angles are 107° , quite close to the theoretical value. Presumably, the unshared pair of electrons occupies a greater volume than does a shared pair, pushing the latter slightly closer together. The arrangement is, therefore, that of a tripod with a hydrogen atom at the end of each leg and the nitrogen atom with its unshared pair sitting at the top (**figure 5.6**). Each nitrogen to hydrogen bond is somewhat polar, making the ammonia molecule polar.

Ammonia, often written NH_3 , is a gas at room temperature. Vast quantities of it are compressed into tanks and used as fertilizer. Ammonia is quite soluble in water. It forms an aqueous solution that is basic; that is, it acts as a base (chapter 7). Such aqueous preparations are familiar household cleansing solutions.

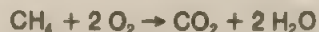
Methane: Marsh Gas as a Perfect Tetrahedron

The element carbon (C) has four electrons in the valence shell of each atom. It can assume the neon configuration by sharing electrons pairs with four hydrogen atoms, thus forming the compound methane.



There are four pairs of electrons on the central carbon atoms in methane. Using the VSEPR theory, we would expect a tetrahedral arrangement and bond angles of 109.5° . The actual bond angles are 109.5° , in perfect agreement with theory (**figure 5.7**). All four electron pairs are shared with hydrogen atoms; thus, all four pairs occupy identical volumes.

Each carbon to hydrogen bond is slightly polar, but the methane molecule as a whole is symmetrical. The slight bond polarities cancel out, leaving the methane molecule, as a whole, nonpolar. Methane often is represented by the formula CH_4 . It is the principal component of natural gas, which is used as a fuel in many parts of the United States. Methane burns with a hot flame, and, if sufficient oxygen is present, the main products (carbon dioxide and water) are relatively innocuous.



Methane is produced by the decay of plant and animal material. It often is seen bubbling to the surface of swamps; hence its common name, marsh gas. Bacterial metabolism in the intestinal tract also produces methane, making methane a major component of intestinal gas.

Some Rules for the Molecular Architect

We have seen in the preceding section how different atoms form different numbers of bonds. Hydrogen forms one bond; chlorine, one; oxygen, two; nitrogen, three; and carbon, four. The number of covalent bonds that an atom can form is called its *valence*. Recall that the lowest energy level of an atom can be occupied by at most two electrons. These may be either shared or unshared. The hydrogen atom has one electron. It can form *one* bond by sharing its electron with another atom. The other atom also furnishes one electron to go with the hydrogen electron and form a shared pair. Hydrogen forms one bond and is said to be *univalent*.

The helium (He) atom has a filled innermost shell. It cannot share electrons with other atoms; hence, its valence is 0.

The second energy level can hold a maximum of eight electrons (i.e., four pairs of electrons). With the element neon (Ne), this shell is filled. Neon has four unshared pairs of electrons and hence forms no bonds. Its valence is 0.

The fluorine (F) atom has seven electrons in its outer, or valence, shell. It can, therefore, form one bond by sharing one electron with another element. The other element furnishes one electron to form a shared pair. So fluorine, like hydrogen, is univalent, having three unshared pairs of electrons and the capacity to form one shared pair.

By similar deductions, we can conclude that oxygen is bivalent, nitrogen is trivalent, and carbon is tetravalent. These rules for molecular architecture are summarized and illustrated in **Table 5.2**. Note that some of the molecules have *multiple bonds* between two atoms. Carbon can form a *double bond* to oxygen by sharing two pairs of electrons. Thus, we can write carbon dioxide as $\text{O}::\text{C}::\text{O}$ or $\text{O}=\text{C}=\text{O}$ (nonbonding electrons are not shown). The two nitrogen atoms in the nitrogen molecule are joined by a *triple bond*; they share three pairs of electrons. We can write the nitrogen molecule as $\text{N}:::\text{N}$ or $\text{N}\equiv\text{N}$.

Now Let's Build Molecules

There is a chemical substance called hydrogen peroxide. Chemical analysis shows that each molecule of it is composed of two hydrogen atoms and two oxygen atoms. This information is indicated in the formula H_2O_2 . What is the structure of the hydrogen peroxide molecule? The parts list is:

2 each H—

2 each O—

↓

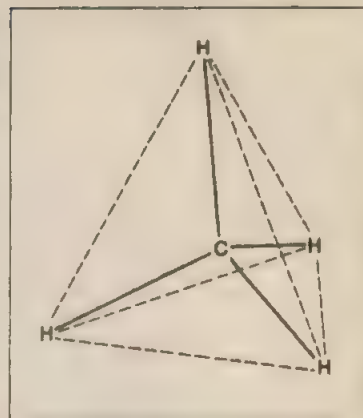
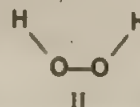
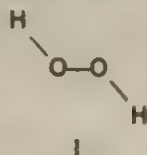


Figure 5.7 The tetrahedral methane molecule. The solid lines indicate covalent bonds; the dotted lines outline the tetrahedron.

Table 5.2
Some Simple Valence Rules

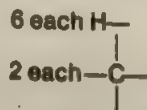
Electron Dot Picture	Valence Bond Picture	Number of Bonds (Valence)	Representative Molecules
H•	H—	1	H—H H— $\ddot{\text{Cl}}$:
He:	—	0	—
• $\ddot{\text{C}}$ •	$\begin{array}{c} \\ \text{—C—} \\ \end{array}$	4	$\begin{array}{cc} \text{H} & :\text{O}: \\ & \\ \text{H—C—H} & \text{C} \\ & :\text{O}: \\ \text{H} & \end{array}$
• $\ddot{\text{N}}$ •	$\begin{array}{c} \ddot{\text{N}} \\ \\ \text{—N—} \\ \end{array}$	3	$\begin{array}{cc} \text{H} & :\text{O}: \\ & \\ \text{H—N—H} & \text{N}\equiv\text{N}: \\ & \\ \text{H} & \end{array}$
• $\ddot{\text{O}}$:	$\begin{array}{c} \ddot{\text{O}} \\ \\ \text{—O:} \\ \end{array}$	2	$\begin{array}{cc} \text{H} & :\text{O}: \\ & \\ \text{H—O:} & \text{C} \\ & \\ \text{H} & \end{array}$
• $\ddot{\text{F}}$:	$\begin{array}{c} \ddot{\text{F}} \\ \\ \text{—F:} \\ \end{array}$	1	H— $\ddot{\text{F}}$: $\ddot{\text{F}}\text{—}\ddot{\text{F}}\text{—}\ddot{\text{F}}$:
• $\ddot{\text{Cl}}$:	$\begin{array}{c} \ddot{\text{Cl}} \\ \\ \text{—Cl:} \\ \end{array}$	1	H— $\ddot{\text{Cl}}$: $\ddot{\text{Cl}}\text{—}\ddot{\text{Cl}}\text{—}\ddot{\text{Cl}}$:

No connections can be made through H, for each H has only one connector. The only kind of molecule that we can make, using all connectors, is I.



Arrangement II, which may look like a different molecule, really isn't. II can be converted into I (and vice versa) by rotation about the O—O bond. (Figure 5.8).

Let's build another molecule. There is a chemical substance called ethane, which, like methane, is a constituent of natural gas. Chemical analysis indicates that ethane molecules are best represented by the formula C_2H_6 . Using the rules of molecular architecture, let's build an ethane molecule. The parts list is:



The only way six Hs and two Cs can be put together according to the rules is

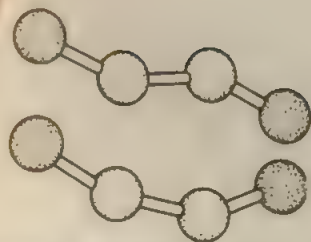
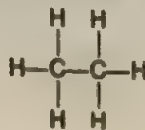


Figure 5.8 Ball-and-stick models of the hydrogen peroxide molecule. One can be made to look like the other by rotation about the bond between the two oxygen atoms.

Actually, methane (CH_4) and ethane (C_2H_6) are merely the first members of a series of similar compounds called *alkanes* or *saturated hydrocarbons*. Other members of the series are discussed in chapter 10.

These rules can be used to construct extremely complicated molecules. You should remember them when writing formulas for covalently bonded compounds.

Problems

- Write electron dot symbols for each of the following elements. You may use a periodic chart.

a. sodium	d. magnesium	g. aluminum
b. fluorine	e. nitrogen	h. potassium
c. carbon	f. oxygen	i. chlorine
- Write electron dot formulas for each of the following.

a. sodium fluoride	d. sodium oxide	g. aluminum nitride
b. potassium chloride	e. sodium nitride	h. aluminum chloride
c. magnesium fluoride	f. magnesium oxide	i. magnesium nitride
- What is the theoretical difference between a sodium atom and a sodium ion? How are the properties of sodium atoms different from those of sodium ions?
- What is the theoretical difference between a chlorine atom, a chlorine molecule, and a chloride ion? How are their properties different?
- What is wrong with the expression "a molecule of sodium chloride"?
- Classify the following bonds as ionic or covalent. For those bonds that are covalent, indicate whether they are polar or nonpolar.

a. KF	d. IBr	g. MgS
b. NO	e. CaO	h. NaBr
c. Br_2	f. F_2	i. HCl
- Use the VSEPR theory to predict the shape of each of the following molecules.
 - a molecule of hydrogen sulfide (H_2S).
 - a molecule of silane (SiH_4).
 - a molecule of beryllium chloride (BeCl_2).
 - a molecule of boron fluoride (BF_3).
- Consider the hypothetical elements X, Y, and Z, which have these electron dot symbols:



- To which group in the periodic table would each belong?
 - Write the electron dot formula for the simplest compound with hydrogen of each. What would be the shape of each of these compounds?
 - Write electron dot formulas for the ions formed when X and Y react with sodium.
 - Write electron dot formulas for compounds formed between X and Y, X and Z, and Y and Z.
- Use the valence rules to construct structural formulas for the following compounds.

a. CH_4O	b. CH_5N	c. NOH_3	d. N_2H_4
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References and Readings

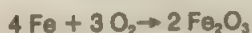
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chapter 6

Names, Formulas, and Equations: You, too, Can Speak Chemistry

Have you ever listened to people speaking a language that you did not understand? To you, it probably seemed just a collection of meaningless sounds, but, to the speakers, the language was perfectly intelligible. The language chemists use is much like a foreign language. An equation like this one:



probably won't mean much to you unless you already have some knowledge of chemical equations. But, if I translated the chemical symbols into English: "iron combines with oxygen (air) to form iron rust," you'd probably understand my meaning.

There are two ways to find out what is being said in a foreign language: you can hire a translator or you can learn to understand the language yourself. To enable you to learn the language of chemistry (so you won't have to depend on a translator), we offer in this chapter a short, intensive course. It won't make you a chemist, but it will make it possible for you to understand a little more of what those mysterious strangers—the chemists—are talking about.

One minor caution before we proceed: the language chemists speak often is closely related to that spoken by mathematicians. Don't worry, though; the math that we use is closely related to the arithmetic you use in everyday life. So hang in there. Before you know it, you, too, will be able to speak the language of chemists.

Names and Symbols for Simple Ions

In chapter 2, you were introduced to chemical symbols. A symbol of one or two letters is used to represent each of the chemical elements. **Table 6.1** lists several common elements and their symbols, some of which are derived from the elements' Latin names. You'll probably save time in the long run if you memorize all or most of them right now.

In the last chapter, we saw how certain metals (those from the left side of the periodic chart) react with nonmetals (those from the right side) to form ionic compounds. Recall that in forming compounds each atom of metal tends to take on

Table 6.1
Some common elements and their symbols



Hydrogen	H	Sulfur	S
Carbon	C	Chlorine	Cl
Nitrogen	N	Potassium (kalium)	K
Oxygen	O	Calcium	Ca
Sodium (natrium)	Na	Iron (ferrum)	Fe
Magnesium	Mg	Copper (cuprum)	Cu
Aluminum	Al	Bromine	Br
Phosphorus	P	Iodine	I

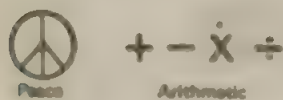


Figure 6.1 The use of symbols is not unique to chemistry. Symbols can be quite helpful when you know what they mean.

enough electrons to complete its valence shell. For example, aluminum atoms with three electrons in their outermost energy levels give up three electrons to form triply charged ions. In electron dot symbols this reaction may be written



Oxygen, with six electrons in its outermost energy level, tends to acquire two more.



The charged atoms formed by the gain or loss of electrons are called *ions*. Table 6.2 lists symbols and names for some simple ions formed in this manner. Note that the

Table 6.2
Symbols and names for some simple ions

Group	Element	Name of Ion	Symbol for Ion
IA	Lithium	Lithium ion	Li^{+}
	Sodium	Sodium ion	Na^{+}
	Potassium	Potassium ion	K^{+}
IIA	Magnesium	Magnesium ion	Mg^{2+}
	Calcium	Calcium ion	Ca^{2+}
IIIA	Aluminum	Aluminum ion	Al^{3+}
VA	Nitrogen	Nitride ion	N^{3-}
VIA	Oxygen	Oxide ion	O^{2-}
	Sulfur	Sulfide ion	S^{2-}
VIIA	Chlorine	Chloride ion	Cl^{-}
	Bromine	Bromide ion	Br^{-}
	Iodine	Iodide ion	I^{-}
IB	Copper	Copper(I) ion (cuprous ion)	Cu^{+}
		Copper(II) ion (cupric ion)	Cu^{2+}
	Silver	Silver ion	Ag^{+}
IIB	Zinc	Zinc ion	Zn^{2+}
VIII	Iron	Iron(II) ion (ferrous ion)	Fe^{2+}
		Iron(III) ion (ferric ion)	Fe^{3+}

charge on an ion of a Group IA element is $1+$ (usually written simply as $+$). The charge on an ion of a Group IIA element is $2+$, and the charge on an ion of a Group IIIA element is $3+$. You can calculate the charge on the negative ions in the table by subtracting 8 from the group number. For example, the charge on the oxide ion (oxygen is in Group VIA) is $6 - 8 = -2$. The charge on a nitride ion (nitrogen is in Group VA) is $5 - 8 = -3$.

There is no simple way to determine the most likely charge on ions formed from Group VIII elements and from those in B subgroups. Indeed, you may have noticed that these can form ions with different charges. In such cases, chemists use roman numerals with the names to indicate the charge. Thus, *iron II ion* means Fe^{2+} and *iron III ion* means Fe^{3+} . In an older system of terminology, Fe^{2+} was called a *ferrous ion* and Fe^{3+} was called a *ferric ion*. See similar terms for the two copper ions in **table 6.2**.

Names of simple positive ions are derived from those of their parent elements by the addition of the word *ion*. A sodium atom (Na), upon losing an electron, becomes a *sodium ion* (Na^+). A magnesium atom (Mg), upon losing two electrons, becomes a *magnesium ion* (Mg^{2+}). Names of simple negative ions are derived from those of their parent elements by the change of the usual ending to *-ide* and the addition of the word *ion*. A chlorine atom (Cl), upon gaining an electron, becomes a *chloride ion* (Cl^-). A sulfur atom (S), upon gaining two electrons, becomes a *sulfide ion* (S^{2-}).

We cannot emphasize too strongly the difference between ions and the atoms from which they are made. They are as different as a whole peach (an atom) and a peach pit (an ion). The names and symbols may look a lot alike, but the substances themselves are quite different. Unfortunately, the situation is confused because people talk about needing "iron" to perk up "tired blood" and "calcium" for healthy teeth and bones. What they really mean is *iron(II) ions* (Fe^{2+}) and *calcium ions* (Ca^{2+}). You wouldn't think of eating iron nails to get "iron." Nor would you eat highly reactive calcium metal. Although careful distinction is not always made by persons who are not chemists, we try to use precise terminology here.

Formulas and Names for Binary Compounds

Simple ions of opposite charge can be combined to form *binary* (two-component) *compounds*. To get the correct formula for a binary compound, simply write each ion with its charge (positive ion to the left) and then cross over the numbers (but not the plus or minus signs) and write them as subscripts. For example, to find the correct formula for calcium chloride, first write the symbols for the ions.



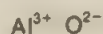
Then cross over the numbers as subscripts:



Then rewrite the formula, dropping the charges. The formula for calcium chloride is:



As a further example consider aluminum oxide. First, write the symbols for the ions:



Cross over the numbers as subscripts:

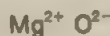


Then rewrite the formula, dropping the charges. The formula for aluminum oxide is:



Please note that the cross-over method works because it is based on the transfer of electrons and the conservation of charge. Two aluminum atoms lose three electrons each (that's six electrons lost) and three oxygen atoms gain two electrons each (that's six electrons gained). Electrons lost equal electrons gained, and all is well. Similarly, two aluminum ions have six positive charges (three each) and three oxide ions have six negative charges (2 each). The net charge on aluminum oxide is 0, just as it should be.

One further example: determine the formula for magnesium oxide. The ions are:



Crossing over, we get



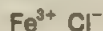
Dropping the charges, we get



Such formulas usually are reduced to the lowest ratio, and we write magnesium oxide as MgO .

Now you are able to translate the "English," such as aluminum oxide, into the "chemistry," Al_2O_3 . You also can translate in the other direction. For example, what is the name corresponding to the formula MgS ? A look at table 6.2 tells us that MgS is made of Mg^{2+} (magnesium ions) and S^{2-} (sulfide ions). The name is simply *magnesium sulfide*.

Let's try another. What is the name for FeCl_3 ? The ions are:



Never mix ammonia and a chlorine bleach--
You'll poison yourself.

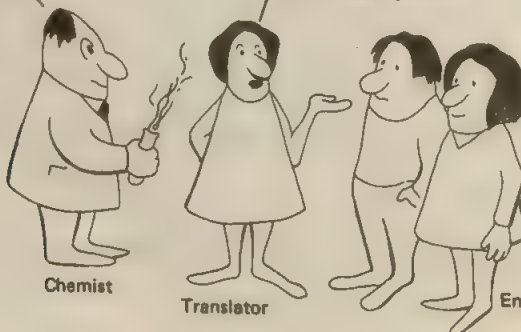


Figure 6.3 Sometimes it helps to translate chemical symbols into English words.

Practice will make you proficient in the language of chemistry just as it will in any other language you are learning. You can gain proficiency by working problems 3 and 4 at the end of this chapter.

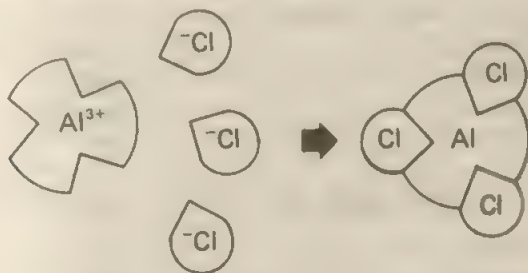
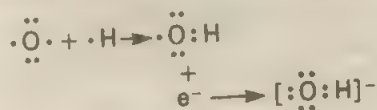
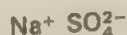


Figure 8.4 One aluminum ion, with three positive charges, can accommodate three chloride ions, each with one negative charge.

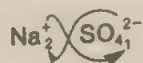
There are many familiar substances (for example, sodium hydroxide, which sometimes is called lye) that have both ionic and covalent bonds. As you might expect, sodium hydroxide contains sodium ions (Na^+). The hydroxide is also an ion; it contains a hydrogen atom covalently bonded to oxygen. There is also an extra electron that gives it a negative charge. We could consider it to have been made by first adding a hydrogen atom and then an electron to an oxygen atom.



As an example, let's write the formula for sodium sulfate. The ions are:



Crossing over, we get



Then, dropping the charges, we have

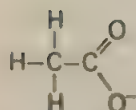


That's easy enough. Now let's do another. What is the formula for ammonium sulfide? The ions are:

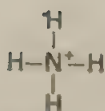


Table 6.3
Some common polyatomic ions

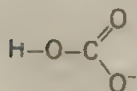
Charge	Name	Formula
1+	Ammonium ion	NH_4^+
1-	Hydrogen carbonate (bicarbonate) ion	HCO_3^-
	Hydrogen sulfate (bisulfate) ion	HSO_4^-
	Acetate ion	CH_3CO_2^- (or $\text{C}_2\text{H}_3\text{O}_2^-$)
	Nitrite ion	NO_2^-
	Nitrate ion	NO_3^-
	Cyanide ion	CN^-
	Hydroxide ion	OH^-
	Dihydrogen phosphate ion	H_2PO_4^-
2-	Carbonate ion	CO_3^{2-}
	Sulfate ion	SO_4^{2-}
	Monohydrogen phosphate ion	HPO_4^{2-}
	Oxalate ion	$\text{C}_2\text{O}_4^{2-}$
3-	Phosphate ion	PO_4^{3-}



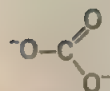
Acetate ion



Ammonium ion



Hydrogen carbonate ion
(bicarbonate ion)

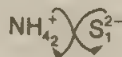


Carbonate ion



Nitrite ion

Crossing over, we get



Dropping the charges gives



Figure 6.5 Polyatomic ions have both covalent bonds (dashes) and ionic charges (+ or -).

The parentheses with a subscript 2 indicate that the entire ammonium unit is taken twice; there are two nitrogen atoms and eight ($4 \times 2 = 8$) hydrogen atoms.

As before, we also can translate in the other direction. What is the name for CaCO_3 ? The ions are Ca^{2+} (calcium ion) and CO_3^{2-} (carbonate ion). The compound is *calcium carbonate*.

One further translation from "chemistry" into "English." What is the name for $\text{Mg}(\text{HCO}_3)_2$? The ions are Mg^{2+} (magnesium ion) and HCO_3^- (hydrogen carbonate, or bicarbonate, ion). The compound is *magnesium hydrogen carbonate*, or *magnesium bicarbonate*.

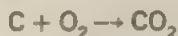
To gain proficiency in writing formulas for compounds containing polyatomic ions, be sure to work problems 5 and 6 at the end of this chapter.

We encounter a few other types of compounds in later chapters. Methods for naming them are explained as they are needed.

The Chemical Equation: A Shorthand Description of Chemical Change

Chemistry is the study of matter and the changes matter undergoes. It is also the study of the energy that brings about those changes in matter—or the energy that is released when those changes occur. So far we have discussed the symbols and the formulas that have been created to represent elements and compounds. Now let's look at a shorthand way of describing chemical changes—the *chemical equation*.

Carbon reacts with oxygen to form carbon dioxide. In chemical shorthand, this reaction is written



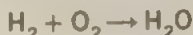
The plus sign (+) indicates the addition of carbon to oxygen (or vice versa) or a mixing of the two in some manner. The arrow (\rightarrow) often is read "yields." Substances on the left of the arrow are called *reactants* or *starting materials*. Those on the right are the *products* of the reaction. The conventions here are like those we used in writing nuclear equations (chapter 4). In these equations, however, the nucleus remains untouched. The chemical reactions we are going to look at involve only electronic structures.

Chemical equations have meaning on the atomic and molecular level. The equation

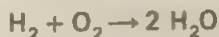


means that one atom of carbon (C) reacts with one molecule of oxygen (O_2) to produce one molecule of carbon dioxide (CO_2).

Not all chemical reactions are so simply represented. Hydrogen reacts with oxygen to form water. We can write this reaction as

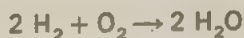


This representation, however, is not consistent with the law of conservation of matter. There are two oxygen atoms shown among the reactants (as O_2) and only one among the products (in H_2O). For the equation to represent correctly the chemical happening, it must be *balanced*. To balance the oxygen atoms we can place the coefficient 2 in front of the formula for water.



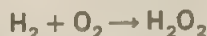
This coefficient means that there are *two* molecules of water involved. As is the case with subscripts, a coefficient of 1 is understood where no other number appears. A coefficient preceding a formula multiplies everything in the formula. In the second equation, the coefficient 2 not only increases the number of oxygen atoms to two, it also increases the number of hydrogen atoms to four.

But that equation is still not balanced. We took care of oxygen at the expense of messing up hydrogen. To balance hydrogen, we place a coefficient 2 in front of the H_2 .



Now there are enough hydrogen atoms on the left. In fact, there are four hydrogens and two oxygens on each side of the equation. Atoms are conserved; the equation is balanced.

Note that we could not balance the equation by changing the subscript for oxygen in water.



The equation would be balanced, but it would not mean "hydrogen reacts with oxygen to form *water*." The formula H_2O_2 represents *hydrogen peroxide*, not water.

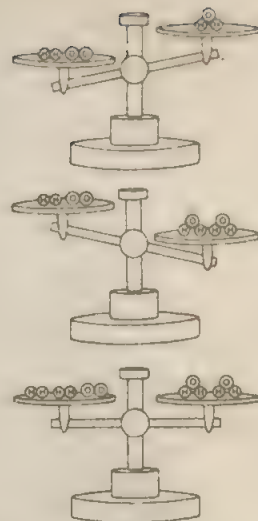


Figure 6.6 To balance the equation for the reaction of hydrogen with oxygen that forms water, the same number of each kind of atom must appear on each side (atoms are conserved). When the equation is balanced, there are four hydrogen atoms and two oxygen atoms on each side.

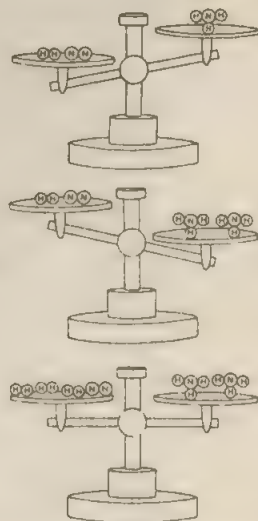
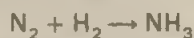


Figure 6.7 To balance the equation for the reaction of nitrogen with hydrogen that forms ammonia, the same number of each kind of atom must appear on each side of the equation. When the equation is balanced, there are two nitrogen atoms and six hydrogen atoms on each side.

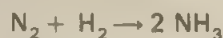
The law of definite proportions tells us that water is always H_2O . We cannot change that merely for the convenience of balancing chemical equations.

Atoms and molecules are rather abstract concepts. Let's try to make balancing equations a little more concrete by use of analogy. Suppose you are making toy wooden bicycles. Each is made of one body and two wheels (just as water is made of one oxygen and two hydrogens). But suppose you could buy bodies and wheels only in packages of two each (just as oxygen atoms and hydrogen atoms come in "packages" [molecules] of two). You could make one bicycle by buying one package of bodies and one package of wheels, but you'd have one body left over—not a very economical way to build bicycles. You could balance things by buying a second package of wheels and building two bicycles. If you are buying parts and selling bicycles, that's the only way to go. You say that you could balance things by building a contraption with two bodies and two wheels? Perhaps you could, but it wouldn't be a bicycle—just as H_2O_2 is not water.

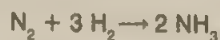
Here's one further example. Balance the equation



You could start in a variety of ways. Perhaps the easiest is to balance nitrogen first by placing the coefficient 2 in front of NH_3 .



That results in six atoms of H on the right side. To get six atoms of H on the left side, we need three molecules of H_2 .

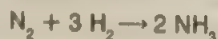


There are two atoms of N and six atoms of H on each side; the equation is balanced.

You can gain proficiency in balancing equations only by practice. Be sure to do problem 7 at the end of the chapter.

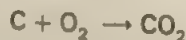
Chemical Arithmetic

Chemical equations give us a count of the atoms and the molecules involved in a chemical change. For example, the equation



tells us that one nitrogen molecule (N_2) reacts with three hydrogen molecules (H_2) to yield two ammonia molecules (NH_3). Each molecule of nitrogen contains two atoms of nitrogen, each molecule of hydrogen contains two atoms of hydrogen, and each molecule of ammonia contains one atom of nitrogen and three atoms of hydrogen. The equation is balanced; atoms are conserved. There are two nitrogen atoms and six hydrogen atoms represented on each side of the equation.

Similarly, the equation



tells us that one atom of carbon reacts with one molecule of oxygen to yield one molecule of carbon dioxide. Each molecule of oxygen contains two atoms of oxygen, and each molecule of carbon dioxide contains one atom of carbon and two of

oxygen. Atoms are conserved in the reaction. The equation is balanced as written because the same number of atoms of each element appears on each side of the equation.

The equation also specifies certain weight relationships. One atom of carbon has a mass of 12 amu and one atom of oxygen has a mass of 16 amu. The equation tells us, therefore, that 12 amu of carbon react with 32 amu (two atoms!) of oxygen to form 44 amu of carbon dioxide. Since atomic mass units are *relative* masses, any other units could be used and the weight relationships would still be valid. Thus, the equation tells us that 12 g of carbon react with 32 g of oxygen to form 44 g of carbon dioxide and that 12 lb of carbon react with 32 lb of carbon to form 44 lb of carbon dioxide. We can use these weight relationships to calculate the amount of reactants required or products produced in chemical reactions.

For example, let's calculate the amount of oxygen that would be required to combine with 24 g of carbon. The equation tells us that 12 g of carbon require 32 g of oxygen. Therefore, 24 g of carbon would require $24 \div 12$, or twice as much oxygen (64 g). Using the unit conversion method,* we would set up the problem like this:

$$24 \text{ g of carbon} \times \frac{32 \text{ g of oxygen}}{12 \text{ g of carbon}} = 64 \text{ g of oxygen}$$

Similarly, we could calculate the amount of carbon dioxide that would be formed by burning 24 g of carbon. The equation tells us that 12 g of carbon form 44 g of carbon dioxide. Therefore, we have:

$$24 \text{ g of carbon} \times \frac{44 \text{ g of CO}_2}{12 \text{ g of carbon}} = 88 \text{ g of CO}_2$$

*If you are not familiar with the unit conversion method of problem solving, see appendix C.

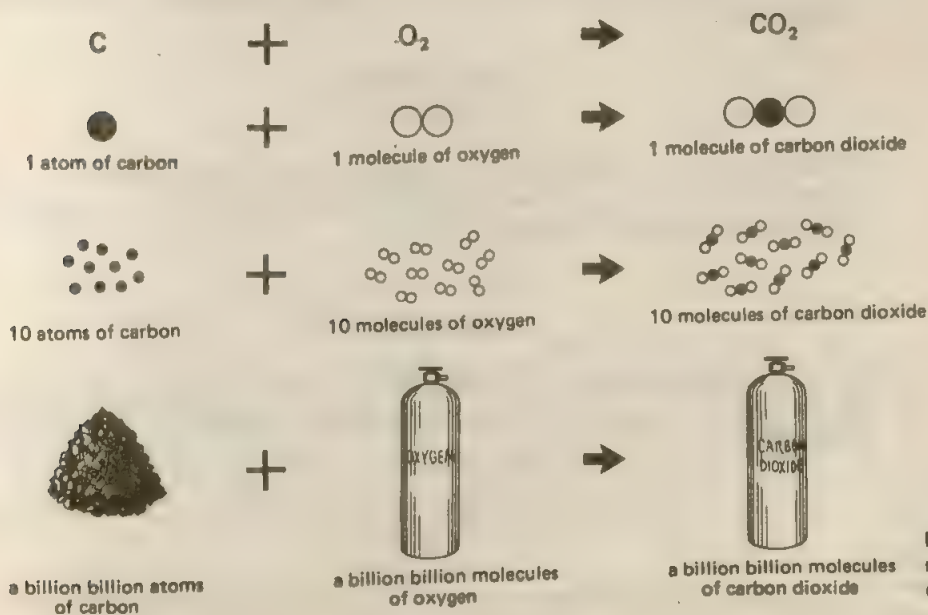


Figure 6.8 Chemical equations represent numbers of atoms and molecules.

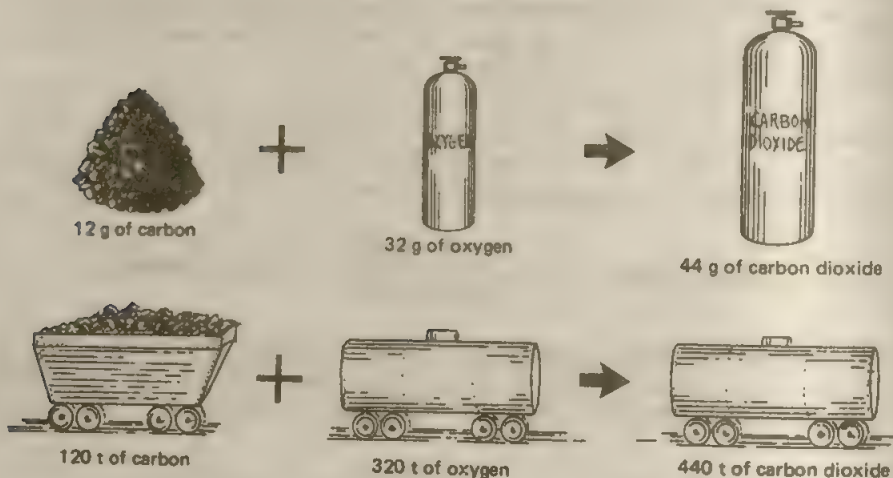
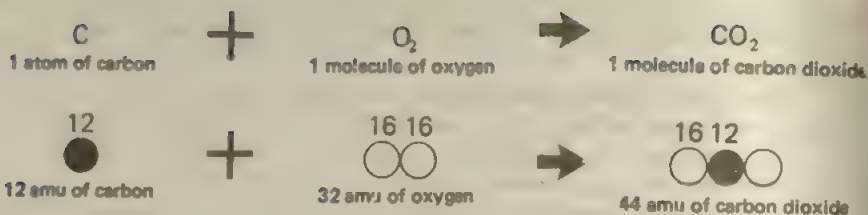
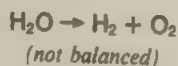


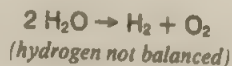
Figure 6.9 Chemical equations express weight ratios as well as numbers of atoms and molecules.

Keep in mind that equations must be balanced before valid weight relationships can be determined. For example, before we can answer the question "how much water must be electrolyzed to produce 100 g of hydrogen?" we must write the equation, balance it, and then do the arithmetic.

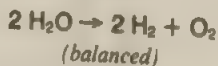
We know that the electrolysis of water produces hydrogen and oxygen. We can therefore write



But the relationship as written is not balanced. There are two oxygen atoms on the right side and only one on the left. *Two* molecules of water are needed to yield the two atoms of oxygen in one molecule of O_2 .



But now the hydrogen is out of balance. There are four hydrogen atoms on the left side and only two on the right. Two molecules of water would produce *two* molecules of hydrogen.



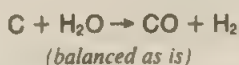
The equation is now balanced, and we can make our calculation. Note that this is exactly the reverse of the reaction of hydrogen and oxygen to form water.

One molecule of water weighs $(2 \times 1) + 16 = 18$ amu. Two molecules of water therefore weigh 36 amu. Two molecules of hydrogen weigh 4 amu. Thus, we know that 36 amu of water would produce 4 amu of hydrogen. To get 100 g of hydrogen, we would have to electrolyze

$$100 \text{ g of H}_2 \times \frac{36 \text{ g of H}_2\text{O}}{4 \text{ g of H}_2} = 900 \text{ g of H}_2\text{O}$$

Now back to the toy bicycle factory. Recall (p. 78) that you can make 2 bicycles from 1 package (of 2) bodies and 2 packages (of 2 each) wheels. Suppose you wanted to make 50 bicycles. Easy enough. You buy 25 packages of bodies (50 bodies) and 50 packages of wheels (100 wheels). Put them together and you have 50 bicycles. But suppose you wanted to make 50 *million* bicycles. Still easy, you say. Just get 25 million packages of bodies (50 million bodies) and 50 million packages of wheels (100 million wheels). But did you ever try counting 25 or 50 million of anything? You've got a bit of a problem. There is another approach to the problem. Say, for example, that each wheel weighs 5 g and each body weighs 40 g. A package of wheels (2 wheels) would weigh 10 g, and a package of bodies (2 bodies) would weigh 80 g. If you need 50 million packages of wheels, just weigh out 500 million g of wheels. If you need 25 million bodies, just weigh out 2000 million g of bodies. Since you can weigh by the truckload (and a truck can easily haul 10 000 000 g, or about 10 metric tons), it is much easier to weigh than to count. And so it is with chemistry. We could get the proper *ratio* of hydrogen to oxygen by taking two molecules of hydrogen (four hydrogen atoms) to one molecule of oxygen (two oxygen atoms). But, since individual molecules are so small, it is convenient to weigh out 4 g of hydrogen and 32 g of oxygen rather than to count those billions of billions of molecules. And we need not take precisely 4 g of hydrogen and 32 g of oxygen as long as the ratio is 4 to 32 (or 1 to 8).

Let's work through another example. One process for the gasification of coal involves the reaction of hot carbon with steam to form carbon monoxide and hydrogen.



How many kilograms of carbon are necessary to produce 10 kg of hydrogen?

The equation tells us that 12 amu of carbon would produce 2 amu of hydrogen. Thus, 12 kg of carbon would yield 2 kg of hydrogen. To obtain 10 kg of hydrogen, we would have to use

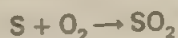
$$10 \text{ kg of H}_2 \times \frac{12 \text{ kg of C}}{2 \text{ kg of H}_2} = 60 \text{ kg of C}$$

Here's one final example. How much sulfur dioxide would be produced by burning 10 kg of coal that contain 3% by weight of sulfur?

First, we should calculate the amount of sulfur in the coal. There would be 3 kg of sulfur in 100 kg of coal. Therefore, in 10 kg of coal there are

$$10 \text{ kg coal} \times \frac{3 \text{ kg of S}}{100 \text{ kg of coal}} = 0.3 \text{ kg of S}$$

Sulfur combines with oxygen to form sulfur dioxide according to the equation



The equation tells us that 32 kg of sulfur would produce $32 + (2 \times 16) = 64$ kg of sulfur dioxide. Therefore, 0.3 kg of sulfur would produce

$$0.3 \text{ kg of S} \times \frac{64 \text{ kg of SO}_2}{32 \text{ kg of S}} = 0.6 \text{ kg of SO}_2$$

If it were advantageous to express the answer in grams, we merely would need to remember that 1 kg is 1000 g:

$$0.6 \text{ kg of SO}_2 \times \frac{1000 \text{ g of SO}_2}{1 \text{ kg of SO}_2} = 600 \text{ g of SO}_2$$

To become proficient in solving problems of this sort, you should work problems 8 through 18. If you have difficulty with them, go back and work through the examples again. If you still have difficulty, seek help from your instructor, tutor, or teaching assistant.

Problems

- Without consulting Tables 6.1 and 6.2, write symbols for each of the following. (You may consult a periodic chart.)

a. carbon	e. potassium	i. aluminum ion
b. calcium	f. phosphorus	j. iron (II) ion
c. chlorine	g. oxide ion	k. bromide ion
d. magnesium	h. sodium ion	l. nitride ion
- Without consulting Tables 6.1 and 6.2, name each of the following.

a. H	e. I	i. Fe^{3+}
b. N	f. Mg^{2+}	j. S^{2-}
c. O	g. I^-	k. Ca^{2+}
d. Fe	h. Cl^-	l. K^+
- Write formulas for the following binary compounds.

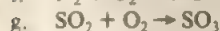
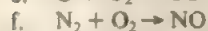
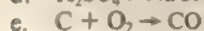
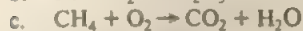
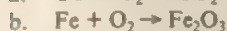
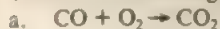
a. sodium bromide	e. iron (II) bromide
b. potassium iodide	f. sodium sulfide
c. calcium oxide	g. magnesium iodide
d. aluminum chloride	h. aluminum oxide
- Name the following binary compounds.

a. NaBr	d. K_2O	g. FeCl_2
b. CaCl_2	e. Na_2S	h. FeCl_3
c. AlI_3	f. Mg_3N_2	i. Fe_2O_3
- Write formulas for each of the following.

a. ammonium chloride	f. calcium hydroxide
b. sodium cyanide	g. magnesium carbonate
c. potassium nitrate	h. sodium sulfate
d. sodium nitrite	i. sodium phosphate
e. sodium hydrogen carbonate (sodium bicarbonate)	
- Name the following compounds.

a. CaSO_4	d. $\text{NaC}_2\text{H}_3\text{O}_2$	g. K_3PO_4
b. K_2CO_3	e. NH_4NO_2	h. $(\text{NH}_4)_2\text{SO}_4$
c. KHCO_3	f. KCN	i. $\text{Al}(\text{OH})_3$

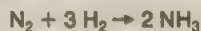
7. Balance the following equations.



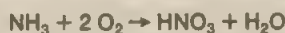
8. What weight of quicklime (calcium oxide) is formed when 100 g of limestone (calcium carbonate) is decomposed by heating?



9. How many grams of hydrogen would be required to produce 68 g of ammonia (NH_3)?



10. Some of the ammonia produced by this process (problem 9) is converted to nitric acid.



How much nitric acid can be made from 68 g of ammonia?

11. Nitric acid is used in the production of trinitrotoluene (TNT), an explosive.



Toluene

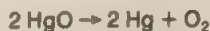
TNT

How much TNT can be made from 46 kg of toluene?

12. The burning of acetylene (C_2H_2) in pure oxygen produces a very hot flame. (This is the reaction in the oxyacetylene torch.) How much oxygen would be required to burn 52 kg of acetylene?



13. Joseph Priestley discovered oxygen in 1774 by using heat to decompose "red calx of mercury," known today as mercury (II) oxide.



How much oxygen is produced by the decomposition of 108 g of HgO ?

14. How much iron can be converted to the magnetic oxide of iron, Fe_3O_4 , by 800 g of pure oxygen?

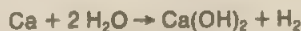


15. Nitrous oxide (laughing gas) can be made by cautiously heating ammonium nitrate.



How much nitrous oxide can be made from 40 g of NH_4NO_3 ?

16. Sometimes a small amount of hydrogen gas is made for laboratory purposes by allowing calcium metal to react with water.



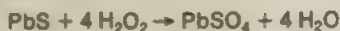
How many grams of hydrogen would be formed by the action of water on 10 g of calcium?

17. For many years it was thought that "inert" gases such as xenon (Xe) would not form chemical compounds. Following Neil Bartlett's breakthrough in 1962, a number of compounds involving "inert" gases have been synthesized. Xenon hexafluoride is made according to the equation:



How many grams of fluorine are required to form 49 g of XeF_6 ?

18. Black lead sulfide (PbS) can be converted to white lead sulfate (PbSO₄) by hydrogen peroxide.



How much hydrogen peroxide would be required to convert 478 mg of PbS to PbSO₄?

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chapter 7

Acids and Bases: Please Pass the Protons

Central to much of the chemistry in our everyday lives is the chemistry of two interrelated classes of compounds called *acids* and *bases*. We use many of these compounds around the house. We clean with ammonia and lye (sodium hydroxide), two familiar bases. We use vinegar (acetic acid) in cooking and as dressing on salads. We take vitamin C (ascorbic acid) and drink beverages made tart by citric acid and phosphoric acid. We treat our excess stomach acid (hydrochloric acid) with a variety of bases, including milk of magnesia (magnesium hydroxide) and baking soda (sodium bicarbonate). Our bodies produce and consume acids and bases, maintaining a delicate balance necessary to our good health and well-being.

Acid rain is an environmental problem in industrialized countries. Bitter, undrinkable alkaline (basic) water is often all that is available in areas with dry climates. Much of our understanding of air and water pollution depends on our knowledge of acids and bases.

In this chapter, we discuss some of the chemistry of familiar acids and bases and some of the properties of these compounds in general. Principles put forth here are used in later chapters. And perhaps of more importance to you is the fact that you will hear and read about acids and bases for all the rest of your life. You will use your knowledge of them every day. Let's hope that what you learn here will enrich your life by giving you a greater understanding of the chemicals that you use and that are a part of your environment.

How to Know an Acid or a Base When You See One

We can define acids and bases in two ways. First, we give an experimental definition. Then, we relate the properties of acids and bases to our knowledge of atoms and molecules in a conceptual definition. And, to simplify things somewhat, we deal only with solutions in water (aqueous solutions).

Experimentally, acids are compounds that would:

1. turn the indicator dye litmus from blue to red;
2. react with active metals (such as iron, tin, and zinc) to dissolve the metal and produce hydrogen gas;

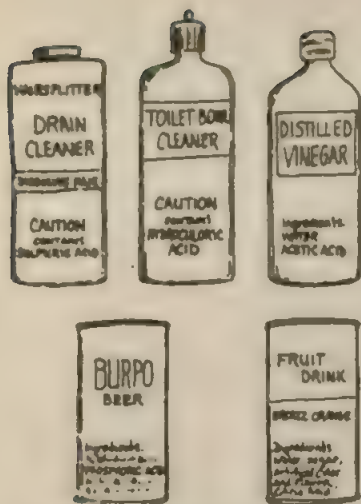


Figure 7.1 Some common acids.

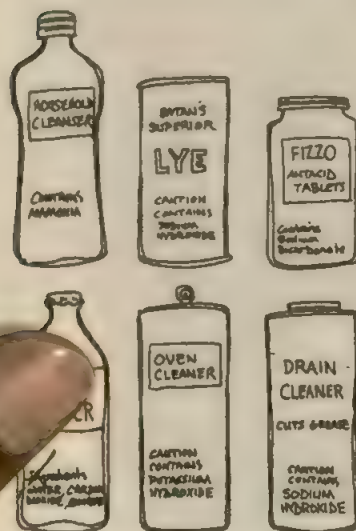


Figure 7.2 Some common bases.

3. taste sour (when diluted enough to be safely tested); and
4. react with bases (or alkalis) to form water and ionic compounds called *salts*.

Similarly, bases are defined experimentally as compounds that, when dissolved in water, would:

1. turn the indicator dye litmus from red to blue;
2. feel slippery or soapy on the skin;
3. taste bitter; and
4. react with acids to form water and salts.

How can you tell when a compound is an acid? You can tell by dissolving some of the compound in water. Since tasting may be hazardous (some acids are poisonous and nearly all are very corrosive unless they have been highly diluted), you can stick a piece of blue litmus paper into a sample of the compound. If the paper turns red, the compound is an acid. Similarly, you can identify a base by dissolving it in water and testing it with red litmus paper. If the paper turns blue, the compound is a base.

You can use a taste test on foods. Many foods are acidic. Vinegar contains 4% to 10% acetic acid. Citrus fruits and many fruit-flavored drinks contain citric acid. If a food tastes sour, most likely it contains one or more acids. Lactic acid is formed in sour milk and is responsible for the tart taste of yogurt. Phosphoric acid is used to impart tartness to beer and some forms of soda pop.

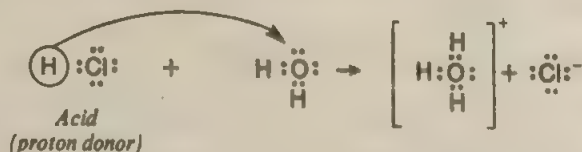
Many medicines taste bitter because they contain alkaloid (alkalilike) compounds. Quinine, caffeine, and the antihistamines are familiar examples.

Acids Explained: Hydronium Ions

It is nice to know that certain compounds are acids and others are bases and that each class has its characteristic properties. It is much more satisfying, however, to know *why* a certain compound is an acid and another a base. The search for meaning is central to science—and to life in general. We will not recount the history of the theory of acids and bases in this discussion, but we will list some of the more important concepts.

A wealth of experimental evidence indicates that, in water solution, the properties of acids are due to H_3O^+ , the *hydronium ion*. This ion is a water molecule to which a hydrogen ion (H^+) has been added. Since a hydrogen atom with its electron removed is just a bare nucleus consisting of a single proton, H^+ often is called a *proton*.

Table 7.1 lists a variety of common acids. Every acid contains one or more hydrogen atoms. When dissolved in water, acids transfer hydrogen nuclei to the water molecules. They are proton donors. For hydrogen chloride, the reaction is written



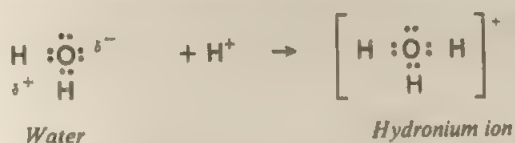
A solution of hydronium ions and chloride ions in water is called *hydrochloric acid*. Other acids react similarly with water to produce hydronium ions.

Yes, it is true, as we mentioned in chapter 5, that oxygen usually forms only two bonds in molecules. Now, in the hydronium ion, it obviously forms three. Why? When you look at the structure of a water molecule, you can see that the oxygen

Table 7.1
Some familiar acids

<i>Name</i>	<i>Formula</i>	<i>Classification</i>
Sulfuric acid	H ₂ SO ₄	Strong
Nitric acid	HNO ₃	Strong
Hydrochloric acid	HCl	Strong
Phosphoric acid	H ₃ PO ₄	Moderate
Lactic acid	CH ₃ CHOHCOOH	Weak
Acetic acid	CH ₃ COOH	Weak
Boric acid	H ₃ BO ₃	Weak
Hydrocyanic acid	HCN	Weak

atom has two unshared pairs of electrons. The oxygen end of the water molecule carries a partial negative charge (chapter 5). Isn't it reasonable to expect that a proton (H⁺), with its positive charge, would stick to the negative end of a water molecule?



Notice that in the hydronium ion, the oxygen atom still has eight electrons in its outer shell (the same structure that neon has). The nice thing, from hydrogen's point of view, is that all three hydrogen atoms now have two electrons in their outer shells (the same structure that helium has). Oxygen doesn't lose its rare gas structure, but the proton is able to gain a rare gas configuration by attaching itself to one of the unshared pairs.

In water, then, the properties of acids are those of the hydronium ion. It is the hydronium ion that turns litmus red, tastes sour, and reacts with active metals, and with bases. Nowadays, however, chemists and other scientists work with solvents other than water. They have broadened the concept of an acid to operate in these other media. Generally speaking, then, an *acid* is a *proton donor*—to any receptor, not just to water.

Bases Explained: Hydroxide Ions

Plenty of experimental evidence indicates that the properties of a base, in water, are due to OH⁻, the *hydroxide ion*. **Table 7.2** lists several common bases. Ionic

Table 7.2
Several common bases

<i>Name</i>	<i>Formula</i>	<i>Classification</i>	Acids and Bases
Sodium hydroxide	NaOH	Strong	
Potassium hydroxide	KOH	Strong	
Calcium hydroxide	Ca(OH) ₂	Moderate	
Magnesium hydroxide	Mg(OH) ₂	Weak	
Ammonia	NH ₃	Weak	

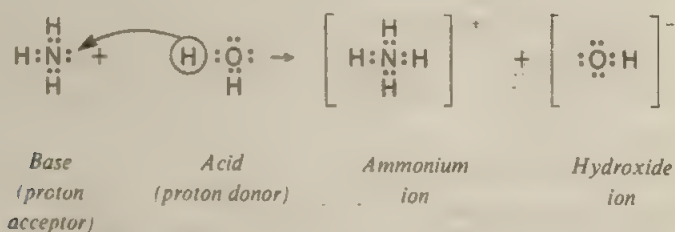
compounds contain two separate and distinct species. In sodium hydroxide, there are sodium ions (Na^+) and hydroxide ions (OH^-). In calcium hydroxide, there are calcium ions (Ca^{2+}) and hydroxide ions (OH^-). When either compound is dissolved in water, a basic solution is formed. The hydroxide ion is the base. Adding sodium hydroxide or calcium hydroxide to water simply supplies an excess of hydroxide ions.

Ammonia seems out of place in the table, because it contains no hydroxide ions. How can it be a base? The only way to get hydroxide ions from ammonia in water is for the ammonia molecule to accept a proton from water, leaving a hydroxide ion.



The NH_4^+ is the ammonium ion.

How can ammonia accept a proton from water? Recall that the nitrogen atom has an unshared pair of electrons. This pair can be used to attach a proton. Removal of a proton from water leaves a hydroxide ion, which is negatively charged because it still has the electrons that bound the "lost" hydrogen.



In water, then, the properties of bases are those of hydroxide ions. The hydroxide ion is a base in water solutions. It turns litmus blue, makes the skin feel soapy, tastes bitter, and reacts with acids. And, just as the concept of an acid has been expanded to include solvents other than water, the definition of a base has been generalized. A base is a *proton acceptor*. This concept includes not only hydroxide ions but also neutral molecules such as ammonia. It also includes other negative ions such as carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), and phosphate (PO_4^{3-}), which, at least to some extent, accept protons in water solution.

Note also that in reacting with ammonia, water acts as a proton donor—an acid. Thus, the idea of an acid as a proton donor and a base as a proton acceptor greatly expands our concept of acids and bases. No longer do we think of an acid simply as a solution of hydronium ions in water and a base as a solution of hydroxide ions in water. The proton donor/acceptor concept is much broader. However, it does include those more limited definitions. It's just that the broader concept is useful in a greater variety of situations.

Acids and Bases: The Strong and the Weak

When gaseous hydrogen chloride (HCl) reacts with water, it does so completely, to give hydronium ions and chloride ions.



In a similar manner, the poisonous gas hydrogen cyanide (HCN) reacts with water to produce hydronium ions and cyanide ions.



However, the reaction in this case takes place only to a slight extent and produces relatively few hydronium ions. Acids that react completely are called *strong acids*. Those that react only slightly are called *weak acids*. Note that Table 7.1 classifies each acid as strong, moderate, or weak. This classification is a measure of the degree of reaction. Strong acids react completely, producing a relatively large number of hydronium ions. Weak acids react only partially, producing fewer hydronium ions.

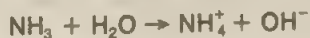
Strong acids, when moderately concentrated, can cause serious damage to skin and flesh. They eat holes in clothes made of natural fibers such as cotton, silk, and wool. Strong acids also destroy most synthetic fibers such as nylon, polyester, and acrylics. Care always should be taken to prevent spills on skin and clothing. In very dilute solutions, strong acids can prove harmless. Hydrochloric acid, for example, is produced in dilute solutions in our stomachs, where it aids in the digestion of certain foodstuffs. Even there, under certain conditions, it can cause problems—as anyone with a ulcer can attest.

Concentrated weak acids can cause problems, too. Although it is pleasant to eat salads with vinegar as a condiment, concentrated solutions of acetic acid are corrosive to the skin and are especially destructive to the lining of the digestive tract.

Bases also are classified as either strong or weak. Perhaps the most familiar strong base is sodium hydroxide (NaOH), sometimes called lye. Even in the solid state, sodium hydroxide is completely ionic; that is, it exists as sodium ions and hydroxide ions. In solution, the hydroxide ions take part in the characteristic reactions that we refer to when we say a solution is basic.

Other common bases include potassium hydroxide (KOH), calcium hydroxide [$\text{Ca}(\text{OH})_2$], and magnesium hydroxide [$\text{Mg}(\text{OH})_2$]. All of these are completely ionic, and yet only potassium hydroxide is classified as a strong base in water solution. Potassium hydroxide, like sodium hydroxide, is quite soluble in water. Therefore, aqueous solutions of the compound are rich in hydroxide ions. Calcium hydroxide is only slightly soluble in water, so the solution contains relatively few dissolved hydroxide ions and is not strongly basic. Magnesium hydroxide is so nearly insoluble that it can be safely taken internally as an antacid (next section).

Ammonia (NH_3) is a familiar weak base. It is a gas at room temperature but readily dissolves in water to yield a basic solution. It reacts with water to a slight extent to produce ammonium ions (NH_4^+) and hydroxide ions.



Ammonia is classified as a weak base for the same reason that magnesium and calcium hydroxide are. An ammonia solution contains relatively low concentrations of hydroxide ions. However, it is not that ammonia is insoluble but rather that once ammonia is in solution it tends *not* to form ions. The solution so formed sometimes is called *ammonium hydroxide*, but, since most of the nitrogen atoms are still in the form of NH_3 , *aqueous ammonia* is perhaps a better name. Many familiar household cleansers contain ammonia, a compound easily detected by its characteristic odor.

As a characteristic property of both acids and bases, we listed the reaction of these compounds with one another to form water and a salt. If a solution containing hydronium ions is mixed with one containing the same amount of hydroxide ions, the resulting solution no longer affects litmus paper. Nor does the new solution taste bitter or sour. The solution is neither acidic nor basic. It is neutral, and the reaction of an acid with a base is called *neutralization*.

Sodium hydroxide reacts with hydrochloric acid to produce water and sodium chloride, a salt (in this case, ordinary table salt).



If equivalent amounts of acid and base are used, the resulting solution is neutral and it tastes salty. The reaction is really that of hydronium ions (acting as an acid) with hydroxide ions (acting as a base) to form water.



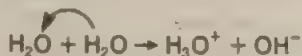
Acid Base
(proton (proton
donor) acceptor)

All Power to the Protons: The pH Scale

It is often convenient in everyday life to count in dozens (a dozen pears, pencils, or people). In chemistry, it is convenient to count in *moles*. A mole is an extremely large number of particles. A mole of a substance is 6.02×10^{23} molecules, atoms, or ions of a substance.

The strength of acid solutions often is measured in moles per litre of solution. A 1 molar (1M) solution of hydrochloric acid contains 1 mole of hydronium ions in each litre of solution. That means 6.02×10^{23} H_3O^+ ions in 1L.

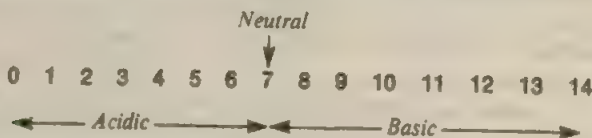
In pure water (or in any neutral aqueous solution), there are 1.0×10^{-7} mole per litre of hydronium ions and an equal number of moles of hydroxide ions. These arise from a slight ionization of water. About 1 molecule in 500 million transfers a proton to another.



Acidic solutions have concentrations of hydronium ions greater than 1.0×10^{-7} mole per litre; basic solutions have concentrations less than 1.0×10^{-7} mole per litre.

Quite frequently, these concentrations are extremely small numbers (in scientific notation, numbers with negative exponents). It is often inconvenient to work with them. In 1909, the Danish chemist S. P. L. Sorensen proposed that only the number in the exponent be used to express acidity. Sorensen's scale came to be known as the pH scale, from the French *pouvoir hydrogene* ("hydrogen power"). On this scale, a concentration of 1×10^{-7} mole of hydronium ions per litre of solution becomes a pH of 7. Similarly, a concentration of 1×10^{-4} mole per litre becomes a pH of 4, and so on.

A pH of 7 represents a neutral solution. A pH lower than 7 means the solution is acidic; a pH higher than 7 indicates that the solution is basic. The *lower* the pH, the more acidic the solution; the *higher* the pH, the more basic the solution.



Each step on the pH scale corresponds to a tenfold change in the concentration of hydronium ions. For example, a solution with a pH of 3 is *10 times* as acidic as a solution with a pH of 4, 100 times as acidic as a solution with a pH of 5, and so on. This relationship will be more evident to you if you keep in mind the corresponding concentrations of hydronium ions. A pH of 3 means a hydronium ion concentration of 1×10^{-3} , or 0.001 mole per litre. A pH of 4 means a hydronium ion concentration of 1×10^{-4} , or 0.0001 mole per litre. Note that 0.001 is 10 times greater than 0.0001.

The relationship between pH and hydronium ion concentration is summarized in table 7.3. The pHs of a variety of common substances are listed in table 7.4.

Table 7.3
The relationship between pH and the concentration of hydronium ions

Concentration of H_3O^+ (in moles per litre)	pH
1×10^0	0
1×10^{-1}	1
1×10^{-2}	2
1×10^{-3}	3
1×10^{-4}	4
1×10^{-5}	5
1×10^{-6}	6
1×10^{-7}	7
1×10^{-8}	8
1×10^{-9}	9
1×10^{-10}	10
1×10^{-11}	11
1×10^{-12}	12
1×10^{-13}	13
1×10^{-14}	14

Table 7.4
The approximate pH of some common solutions

Solution	pH
Hydrochloric acid (4%)	0
Gastric juices	1.6-1.8
Lemon juice	2.3
Vinegar	2.4-3.4
Soft drinks	2.0-4.0
Milk	6.3-6.6
Urine	5.5-7.0
Rainwater (unpolluted)	6.2
Saliva	6.2-7.4
Pure water	7.0
Blood	7.35-7.45
Fresh egg white	7.6-8.0
Bile	7.8-8.6
Milk of magnesia	10.5
Washing soda	12.0
Sodium hydroxide (4%)	13.0

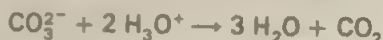
An Acid-Base Laboratory: Your Stomach

The stomach secretes hydrochloric acid (HCl) to help in the digestion of food. Sometimes overindulgence or emotional stress lead to a condition called *hyperacidity* (too much acid). A number of antacids that treat this condition are available, many of them aggressively advertised. Indeed, sales of antacids in the United States were

estimated to be \$117 million in 1972. Let's look at some popular antacids from the standpoint of acid-base chemistry.

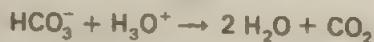
Tums, a familiar antacid tablet, contains calcium carbonate (CaCO_3), magnesium carbonate (MgCO_3), and magnesium trisilicate ($\text{Mg}_2\text{Si}_3\text{O}_8$). Calcium carbonate, an effective antacid, is also an antidiarrheal. Magnesium carbonate, used as an antacid in small doses, is an effective laxative in large doses. Magnesium trisilicate is used in the treatment of ulcers and gastritis.

Rolaids, often boasted of as consuming 47 times its weight in "stomach acid," has aluminum sodium dihydroxy carbonate [$\text{AlNa}(\text{OH})_2\text{CO}_3$] as the only active ingredient. (See reference 3 for an interesting study of Rolaids' advertising claim.) Both the hydroxide ion (OH^-) and the carbonate ion (CO_3^{2-}) consume acid (H_3O^+ ions)—that is, they act as bases.



Maalox, in the form of an aqueous suspension, contains magnesium hydroxide [$\text{Mg}(\text{OH})_2$] and aluminum hydroxide [$\text{Al}(\text{OH})_3$]. The former is an antacid and a laxative, the latter is an antacid and is antidiarrheal. How's that for balance?

Alka-Seltzer, often recommended for overindulgence and upset stomach, contains calcium dihydrogen phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2$], sodium bicarbonate (NaHCO_3), citric acid, and aspirin. The familiar fizz is due to the carbon dioxide gas released by the reaction of bicarbonate ions with the acidic components when dissolved.



Note that bicarbonate ions act as bases. *Alka-Seltzer* came under attack when it was pointed out that the aspirin in it might be harmful to people with ulcers and other stomach disorders. To offset that criticism, the makers introduced *Alka-Seltzer Gold*, which does not contain aspirin. Only the fizz-making ingredients are left.

Figure 7.3 A selection of antacids offered to the public. All are basic compounds. (Photo by Dennis Tasa.)

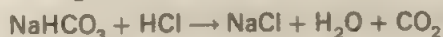
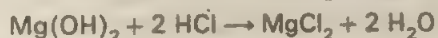
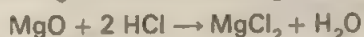


Probably the cheapest and most effective antacid is calcium carbonate (CaCO_3), commonly called *precipitated chalk*. The compound, however, causes constipation in some people. There is also recent evidence that shows that calcium ions (Ca^{2+}) actually trigger the release of *more* hydrochloric acid, leading to an "acid rebound" worse than the original hyperacidity.

Milk of magnesia, a suspension of magnesium hydroxide [$\text{Mg}(\text{OH})_2$] in water, serves as a laxative in large doses and as an antacid in lower doses. It is sold under a variety of brand names. Sodium bicarbonate, or baking soda (NaHCO_3), is safe for occasional use. Overuse can make the blood too alkaline, a condition called *alkalosis*. Also, the sodium ion must be avoided by people with hypertension.

Other indigestion remedies contain still other drugs. *Bromo-Seltzer* once contained, among other things, potassium bromide (KBr). According to *The Merck Index* (reference 8), large doses of potassium bromide cause depression of the central nervous system. Prolonged intake can cause mental deterioration and acneform skin eruptions. *Bromo-Seltzer*, despite its name, no longer contains potassium bromide. The pain reliever currently in it is acetaminophen, an aspirin substitute. *Pepto-Bismol* is an antacid preparation that also contains an antidiarrheal drug.

The main ingredient of any antacid preparation is a basic compound, that is, some compound that neutralizes acids. The acid-base chemistry of antacids is summarized in the following reactions.



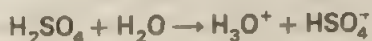
Notice that in each case the products are a compound of a metal and the nonmetal chlorine—a salt—and water. The carbonates and bicarbonates form carbon dioxide as an additional product. Since extra ingredients add little—except cost—to antacid preparations, you can choose your base on the basis of price.

Anyone with severe or repeated attacks of indigestion should consult a physician. Self-medication in such cases could be dangerous.

Acids, Bases, and Human Health

Strong acids and bases cause damage on contact with living cells. Their action is nonspecific. All cells, regardless of type, are damaged more or less equally. These *corrosive* poisons produce what are known as chemical burns. The injuries, once the offending agent is neutralized or removed, are quite similar to burns from heat. They often are treated the same way.

Sulfuric acid (H_2SO_4) is by far the leading chemical product of United States industry. About 36 billion kg were produced in 1978. Most is used by industries. Only a small portion is used in or around the house. Automobile batteries contain sulfuric acid. Sulfuric acid is also the major ingredient in one type of drain cleaner, presumably because it dissolves drain-clogging hair. Sulfuric acid is a powerful dehydrating agent. It takes up water from cellular fluid, rapidly killing the cell. The sulfuric acid molecules dehydrate by actually reacting with water in the cells to form hydronium ions and hydrogen sulfate ions.



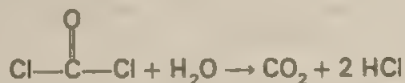
Hydration of these ions and other secondary reactions may also be involved in the dehydration process.

The burning of sulfur-containing coal produces aerosol mists of sulfuric acid. The effects on the environment and human health of acid air pollutants are discussed in chapter 19.

Hydrochloric acid (also called muriatic acid) is used in homes to clean calcium carbonate deposits from toilet bowls. It is used in building construction to remove excess mortar from bricks. In industry, it is used to remove scale or rust from metals. Concentrated solutions (about 38% HCl) cause severe burns, but dilute solutions are considered safe enough for use around the house. Even dilute solutions, however, can cause skin irritation and inflammation.

Ingestion of sulfuric, hydrochloric, or any other strong acid causes corrosive damage to the digestive tract. As little as 10 ml of concentrated (98%) sulfuric acid, taken internally, can be fatal.

Phosgene, used in gas warfare during World War I, acts by reacting with moisture in the lungs to produce hydrochloric acid.



The irritated lung tissue gives up water to the dehydrating acid, and the lungs fill with fluid. The victim dies of suffocation.

Sodium hydroxide (lye) is by far the most common of the strong bases used for household purposes. It is used to open clogged drains and as an oven cleaner. It destroys tissue rapidly, causing severe chemical burns.

Several detergent additives—such as carbonates, silicates, and borates—form strongly basic solutions when dissolved in water. These, too, can cause corrosive damage to tissues, particularly those of the digestive tract and the eyes.

Both acids and bases, even in dilute solutions, break down the protein molecules in living cells. Generally, the fragments are not able to carry out the functions of the original proteins. In cases of severe exposure, the fragmentation continues until the tissue has been completely destroyed. And, within living cells, proteins function properly only at an optimum pH. If the pH changes much in either direction, the proteins can't carry out their usual functions properly.

When they are misused, acids and bases can be damaging to human health. But acids and bases affect human health in more subtle—and ultimately more important—ways. A delicate balance must be maintained between acids and bases in the blood and body fluids. If the acidity of the blood changes very much, it loses its capacity to carry oxygen. Fortunately, the body has a complex but efficient mechanism for maintaining proper acid-base balance. A study of that mechanism is beyond the scope of this book. Interested readers are urged to consult reference 1 for an explanation of this mechanism.

Problems

1. List four general properties of acidic solutions.
2. List four general properties of basic solutions.
3. What ion is responsible for the properties of acidic solutions (in water)?
4. What ion is responsible for the properties of basic solutions (in water)?
5. Give the formulas and the names of two strong acids and two weak acids.
6. Give the formulas and the names for two strong bases and two weak bases.
7. Magnesium hydroxide is completely ionic, even in the solid state, and yet it can be taken internally as an antacid. Explain why it does not cause injury as a strong base would

8. Give a general definition for an acid. Write an equation that illustrates your definition.
9. Indicate whether each of the following pH values represents an acidic, a basic, or a neutral solution.
 - a. 4
 - b. 7
 - c. 3.5
 - d. 9
10. Examine the labels of at least five antacid preparations. Make a list of the ingredients in each. Look up the properties (medical use, side effects, toxicity, etc.) of each ingredient in a reference book such as *The Merck Index*.
11. Give two ways in which corrosive acids and alkalies destroy cells.
12. How does phosgene exert its damaging effect?
13. Identify the actual proton donors and acceptors in the reactions on p. 93.

References and Readings

1. Hill, John W., and Feigl, Dorothy M., *Chemistry and Life*, Minneapolis: Burgess, 1978. See especially chapters 10 and 11.
2. Jaffe, Bernard, *Crucibles: The Story of Chemistry*, New York: Fawcett World Library, 1957. Chapter 10 relates the work with acids, bases, and salts of Svante Arrhenius.
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chapter 8

Oxidation and Reduction: Burn and Unburn

Life is a battle between two competing chemical processes, *oxidation* and *reduction*. We are constantly losing the battle—nothing lives forever. The decay of plants, the energy-supplying reactions that enable us to grow older, and the ultimate corruption of our bodies all involve oxidation. We are, nonetheless, fighting a magnificent delaying action. Green plants keep us in the battle by reversing oxidation. They carry out reduction reactions in which, by means of energy captured from sunlight, carbon dioxide is reduced to high-energy carbon compounds such as sugars. It is this trapped solar energy, stored in our foods as chemical energy, that ultimately supports all life as we know it.

Farmers use their own muscular energy, that of domesticated animals, and the stored energy of fossil fuels (coal and petroleum products) to grow plants that support much of human life. Yet, even this assistance depends ultimately on the plants themselves, those that feed the farmers and their livestock and those that were buried eons ago and eventually formed the fossil fuels. Reduced forms of carbon compounds—sugars, coal, gasoline—are high in energy. Oxidized forms—carbon dioxide and water—are low in energy.

In this chapter, we study the processes of oxidation and reduction that enable plants to provide us with energy-rich substances and also enable us to use those substances to obtain the energy necessary for our survival.

Oxygen: Abundant and Essential

It would be inaccurate to say that any one element is the most important one, for there are 20 or so elements essential to life. Nevertheless, in any list of important elements, oxygen would be at or near the top. It is an abundant element, making up about half the Earth's crust. Oxygen occurs in each of the three subdivisions of the crust—the atmosphere, the hydrosphere, and the lithosphere. It occurs in the *atmosphere* (the gaseous mass surrounding the Earth) as molecular oxygen (O_2). In the *hydrosphere* (the oceans, seas, rivers, and lakes of the Earth), oxygen occurs in combination with hydrogen in the remarkable compound, water (H_2O). In the *lithosphere* (the solid portion of the Earth), oxygen occurs in combination with silicon (pure sand is largely SiO_2) and a variety of metals.

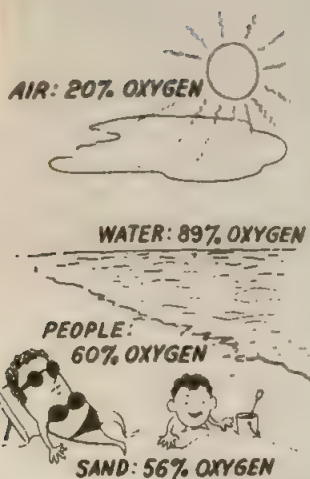


Figure 8.1 Oxygen is the most abundant element in the Earth's crust.

Oxygen is found in most of the compounds that are important to living organisms. Foodstuffs—carbohydrates, fats, and proteins—all contain oxygen. The human body is approximately 65% (by weight) water. Since 89% of the weight of water is due to oxygen—and many other compounds in our bodies also contain oxygen—over 60% of the weight of each one of us is oxygen.

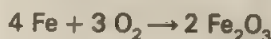
Elemental oxygen (O_2) accounts for about 21% (by volume) of the atmosphere. (The remainder is mainly nitrogen (N_2), which enters into few chemical reactions.) Atmospheric oxygen is said to be free or uncombined, that is, not part of a compound containing another element. Oxygen (in air) is taken into the lungs. From there it passes into our bloodstreams. The blood carries oxygen to the body tissues, and the food we eat combines with this oxygen. This chemical process provides us with energy in the form of heat to maintain our body temperature. It also gives us the energy we need for mental and physical activity.

Oxygen performs many other functions. Fuels such as natural gas, gasoline, and coal need oxygen in order to burn and release their stored energy. Combustion of fossil fuels currently supplies over 90% of the energy that turns the wheels of civilization.

Not all that oxygen does is immediately desirable. Oxygen causes iron to rust and copper to corrode, and it aids in the decay of wood. All these—and many other—chemical processes are called oxidation.

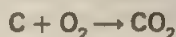
Chemical Properties of Oxygen: Oxidation

When iron rusts, it combines with oxygen from the atmosphere to form a reddish brown powder.

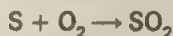


The chemical name for iron rust (Fe_2O_3) is iron(III) oxide. Sometimes it also is called by an older name, ferric oxide. Many other metals react with oxygen to form *oxides*.

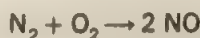
Most nonmetals also react with oxygen to form oxides. For example, carbon reacts with oxygen to form carbon dioxide.



Sulfur combines with oxygen to form sulfur dioxide.

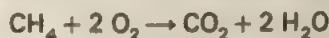


And, at high temperatures (such as those that occur in automobile engines), even nitrogen, which is ordinarily quite unreactive, combines with oxygen.



The product is known as nitric oxide.

Oxygen also reacts with many compounds. Methane, the principal ingredient in natural gas, burns in air to produce carbon dioxide and water.



Hydrogen sulfide, a gaseous compound with a rotten egg odor, burns, producing water and sulfur dioxide.

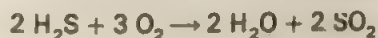
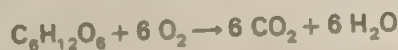


Figure 8.2 Cooking, breathing, and burning fuel all involve oxidation.

In each example, oxygen combines with each of the elements in the compound.

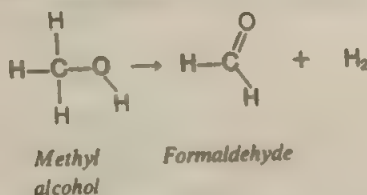
The combination of elements and compounds with oxygen is called oxidation. The substances that combine with oxygen are said to have been *oxidized*. Originally, the term *oxidation* was restricted to reactions involving combination with oxygen. Chemists came to recognize, though, that combination with chlorine (or bromine or other elements in the upper-right portion of the periodic chart) was not all that different from reaction with oxygen. So they broadened the definition of oxidation. We won't concern ourselves, though, with a formal definition. The three following working definitions should suffice.

1. An element or a compound is oxidized when it gains oxygen atoms. In the reactions we've encountered so far in this section, iron, carbon, sulfur, nitrogen, methane, and hydrogen sulfide all gain oxygen atoms. We say, then, that each of these substances is oxidized. Consider also the "burning" of glucose by living cells. This process, called *respiration*, is the main reaction by which cells obtain energy.



In the reaction, carbon atoms gain oxygen. Each has one oxygen in glucose but two in carbon dioxide (figure 8.3). Glucose is oxidized.

2. A compound is oxidized when it loses hydrogen atoms. Methyl alcohol, when passed over hot copper gauze, forms formaldehyde and hydrogen gas.



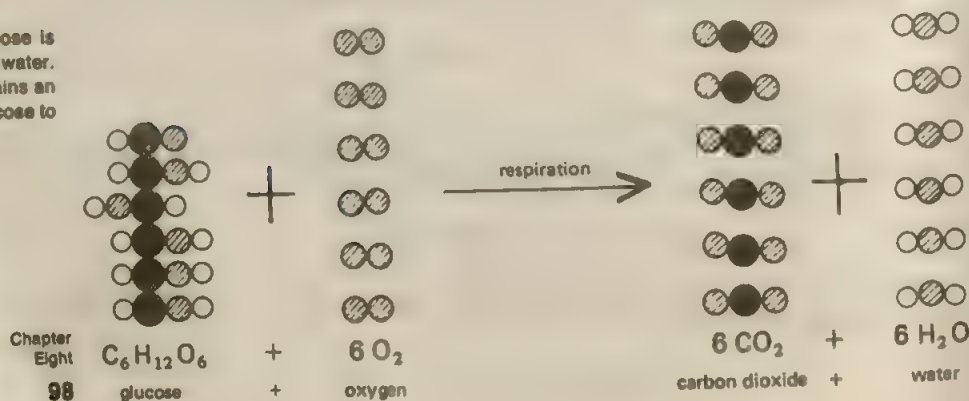
Since methyl alcohol loses hydrogen atoms, it is said to have been oxidized.

3. An element is oxidized when it loses electrons. When magnesium metal reacts with chlorine, magnesium ions and chloride ions are formed.



Since the magnesium atom obviously loses electrons, it is oxidized.

Figure 8.3 In respiration, glucose is oxidized to carbon dioxide and water. Note that each carbon atom gains an oxygen atom in going from glucose to carbon dioxide.



We encounter many reactions that fit these definitions in subsequent sections of this book. For example, it is by oxidation of foodstuffs that organisms derive their life-sustaining energy. Our bodies also oxidize toxic molecules, making them more polar, in order to eliminate them in urine, an aqueous solution.

Why so many different definitions of oxidation? Simply for convenience. Which do we use? Whichever is most convenient. For the reaction



it is convenient to see that carbon is oxidized, because it gains oxygen atoms. Similarly, for the reaction



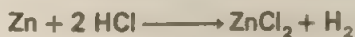
it is easy to see that carbon is oxidized, because it loses hydrogen atoms.

Hydrogen: Lots but Light

For every oxidation process, there is a complementary process—reduction. Before discussing reduction in detail, let's look at some of the chemistry of another important element—hydrogen.

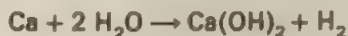
By weight, hydrogen makes up only about 0.9% of the Earth's crust, so hydrogen is placed far down on the list of abundant elements.* However, hydrogen atoms are quite abundant since hydrogen is the lightest element. If we considered a random sample of 10,000 atoms from the earth's crust, 5330 would be oxygen atoms, 1590 would be silicon atoms, and 1510 would be hydrogen atoms. Unlike oxygen, hydrogen is seldom found free in nature on Earth. Most of it is combined with oxygen in water. Nearly all compounds derived from living organisms contain hydrogen. Fats, starches, sugars, and proteins all contain combined hydrogen. Petroleum and natural gas are mixtures composed mainly of *hydrocarbons*, compounds of hydrogen and carbon (chapter 10).

Since elemental hydrogen does not occur in nature (again, we limit our view to this planet), it is necessary for humans to manufacture it. Small amounts can be made for laboratory use by the reaction of zinc with hydrochloric acid



Zinc
chloride

or by the reaction of calcium metal with water:



Calcium
hydroxide

Gaseous hydrogen can be easily collected by displacement of water.

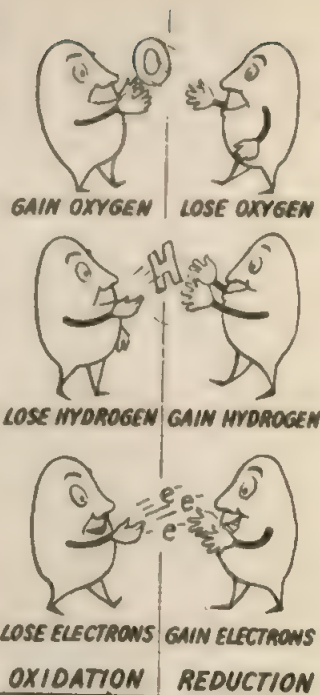
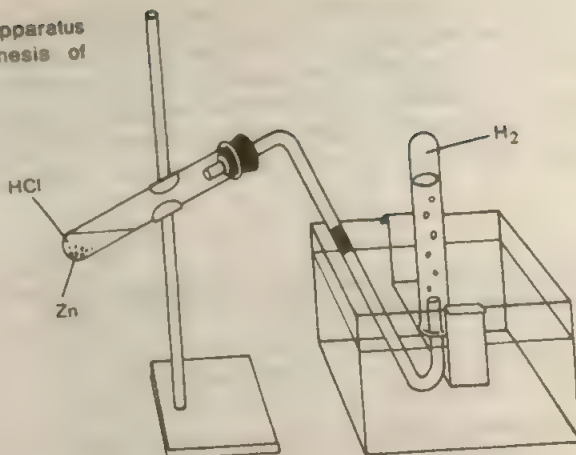


Figure 8.4 Oxidation and reduction can be defined in a variety of ways.

*Hydrogen ranks low in abundance on Earth. If we look beyond our home planet, however, hydrogen becomes much more significant. The sun, for example, is made up largely of hydrogen. In fact, in the universe, hydrogen is by far the most abundant element.

Figure 8.5 A diagram of an apparatus for the laboratory synthesis of hydrogen.



Commercially, hydrogen usually is obtained as a by-product of other processes. Much of it comes from the *cracking* of petroleum, a process by which oils that boil at high temperatures are converted to lower-boiling fuels, such as gasoline.

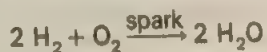
Physically, hydrogen is a colorless and odorless gas. It is essentially insoluble in water. Hydrogen is the least dense of all substances; its density is only about 14% that of air under comparable conditions. For this reason, it was at one time used in zeppelins (dirigibles) to give them the necessary buoyancy in air. However, since a spark or a flame can trigger the explosion of hydrogen, the use of this gas represented a considerable danger. When a disastrous explosion occurred aboard a luxury airship, the *Hindenburg*, in 1937, the use of hydrogen was discontinued and so too was the commercial use of lighter-than-air ships. Dirigibles (for example, blimps) in use today employ the nonreactive gas helium, while hot-air balloons use (as their name indicates) hot air, which is less dense than the cooler atmosphere.

Certain metals, such as platinum (Pt), palladium (Pd), and nickel (Ni), collect large volumes of hydrogen (in a condensed form) on their surfaces. This *adsorbed* hydrogen appears to be a great deal more reactive than ordinary molecular hydrogen; thus, these metals often are used as catalysts* for reactions involving H_2 as one of the reactants.

*A *catalyst* is a substance that increases the *rate* of a chemical reaction without itself being used up. For example, sulfuric acid increases the *rate* at which normal alkanes (chapter 10) are converted to branched structures. It does not, however, increase the *percentage* of conversion.

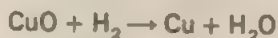
The Chemical Properties of Hydrogen: Reduction

Chemically, a jet of hydrogen, when ignited, burns in air with an almost colorless flame. Hydrogen and oxygen can be mixed at room temperature with no perceptible reaction. However, when the mixture is ignited by a spark or a flame, a tremendous explosion results. The product in both cases is water.

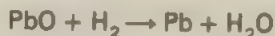


platinum acts as a catalyst; it lowers the activation energy for the reaction. The platinum glows from the heat released in the initial reaction and then ignites the mixture, causing an explosion.

Hydrogen reacts with a variety of metal oxides to remove oxygen and give the free metal. For example, when hydrogen is passed over heated copper oxide, metallic copper and water are formed.



With lead oxide, the products are metallic lead and water.



This process, in which a compound is changed or reduced to an element, is labeled reduction.

Like *oxidation*, which once meant simply the combination of an element or a compound with oxygen, the term *reduction* has a broadened meaning. Instead of a formal definition, however, we use working definitions like those given for oxidation.

1. A compound is reduced when it loses oxygen atoms. In the examples above, CuO and PbO obviously were reduced, since they lost oxygen. When potassium chlorate (KClO_3) is heated, it forms potassium chloride and oxygen gas.



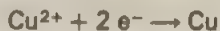
The potassium chlorate loses oxygen; therefore, it is reduced.

2. A compound is reduced when it gains hydrogen atoms. For example, methyl alcohol is made by reaction of carbon monoxide (CO) with hydrogen.



The carbon monoxide gains hydrogen; therefore, it is reduced.

3. An atom or an ion is reduced when it gains electrons. When an electric current is passed through a solution containing copper ions (Cu^{2+}), copper metal is plated out at the cathode.



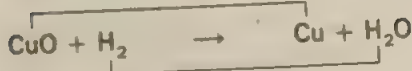
The copper ion obviously gains electrons; therefore, it is reduced.

Oxidation and reduction go hand in hand. You can't have one without the other. When one substance is oxidized, another is reduced. For example, in the reaction



copper oxide is reduced and hydrogen is oxidized. Further, if one substance is being oxidized, the other must be causing it to be oxidized. In the example, CuO is causing H_2 to be oxidized. Therefore, CuO is called the *oxidizing agent*. Conversely, H_2 is causing CuO to be reduced, so H_2 is the *reducing agent*. Each *oxidation-reduction* (sometimes called *redox*) *reaction* has an oxidizing agent and a reducing agent among the reactants. The *reducing agent* is the substance being *oxidized*; the *oxidizing agent* is the substance being *reduced*.

Reduction:
copper oxide is being reduced;
CuO is the oxidizing agent.

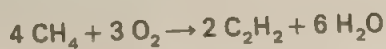


Oxidation:
hydrogen is being oxidized;
H₂ is the reducing agent.

Some Friendly Neighborhood Oxidizing Agents

Oxygen is undoubtedly the most common oxidizing agent. It oxidizes the wood in our campfires and the gasoline in our automobile engines. It rusts and corrodes the metals that we get by reducing ores. It even "burns" the foods we eat to give us energy to move and to think. It is involved in the rotting of wood and the weathering of rocks. Indeed, we live in an oxidizing atmosphere. Fortunately, though, oxygen is a mild oxidizing agent; otherwise, living things would burn up quickly. As it is, it takes us about 70 years to "burn out."

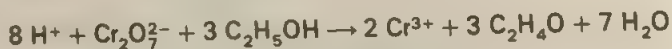
Oxygen sometimes is used as a laboratory and industrial oxidizing agent. For example, acetylene (used to fuel cutting and welding torches) is made by the partial oxidation of methane.



Methane

Acetylene

(Complete oxidation of methane gives carbon dioxide and water.) Often, though, it is more convenient to use other oxidizing agents. In the laboratory, sodium dichromate (Na₂Cr₂O₇) is used frequently to oxidize alcohols to compounds called *aldehydes* and *ketones*. For the oxidation of ethyl alcohol (found in alcoholic beverages) to acetaldehyde, the reaction is:



Dichromate ion
(orange-red)

Chromium(III) ion
(green)

Some of the tests for intoxication (the breathalyzer used to test drunken drivers, for instance) depend on the oxidation of alcohol by an oxidizing agent that changes color as it is reduced (such as a chromium compound).

Another common oxidizing agent is hydrogen peroxide, H₂O₂. Pure hydrogen peroxide is a syrupy, colorless liquid. It usually is used as an aqueous solution, with concentrations of 30% and 3% generally available. Some interesting uses of hydrogen peroxide are discussed in the next section. For now, let's look at some of its simpler chemistry.

Hydrogen peroxide oxidizes sulfides (S²⁻) to sulfates (SO₄²⁻). When lead-based paints are exposed to polluted air containing hydrogen sulfide (H₂S), they turn black because of the formation of lead sulfide (PbS). Hydrogen peroxide oxidizes the black sulfide to the white sulfate.

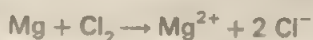


(Black)

(White)

A nice advantage of hydrogen peroxide as an oxidizing agent is that it is converted to water, an innocuous by-product, in most reactions.

Other common oxidizing agents are the halogens—fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). Chlorine, for example, oxidizes magnesium metal to magnesium ions.



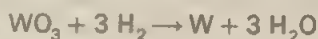
We encounter still other interesting oxidizing agents as we go along.

Some Reducing Agents of Interest

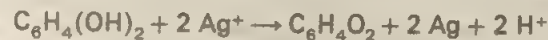
There is no single reducing agent that stands out as oxygen does among oxidizing agents. Hydrogen reduces many compounds, but it would be rather expensive for large-scale processes. Elemental carbon (as coke obtained by driving off the volatile matter from coal) is used frequently to obtain metals from their ores. For example, tin can be obtained from tin oxide by reduction, with carbon used as the reducing agent.



Hydrogen can be used for the production of expensive metals, such as tungsten (W). First, the tungsten ore is converted to an oxide (WO_3), and then it is reduced in a stream of hydrogen gas at $1200^\circ C$.



Perhaps a more familiar reducing agent, by use if not by name, is the developer used in photography. Photographic film is coated with a silver salt, $Ag^+ Br^-$. Silver ions that have been exposed to light react with the developer, a reducing agent (such as the organic compound hydroquinone), to form metallic silver.



Hydroquinone

*Silver
metal*

Those silver ions that were not exposed to light are not reduced by the developer. The film is then treated with "hypo," a solution of sodium thiosulfate ($Na_2S_2O_3$), which washes out unexposed silver bromide. That leaves the negative dark where the metallic silver has been deposited (where it was originally exposed to light) and transparent where light did not strike it. Light shone through the negative onto light-sensitive paper then makes the positive print.

Oxidation and Antiseptics

Many common antiseptics (compounds that are applied to living tissue to kill microorganisms or to prevent their growth) are mild oxidizing agents. Hydrogen peroxide (H_2O_2), in the form of a 3% aqueous solution, finds use in medicine as a topical antiseptic. It can be used to treat minor cuts and abrasions on certain parts of the body. Potassium permanganate, in concentrations ranging from 0.01% to 0.2%, can be used as a topical antiseptic and astringent. Potassium chlorate ($KClO_3$) was once used as an antiseptic for skin and mucous membranes. Its use has been largely discontinued because it is rather irritating, somewhat toxic, and only marginally effective.

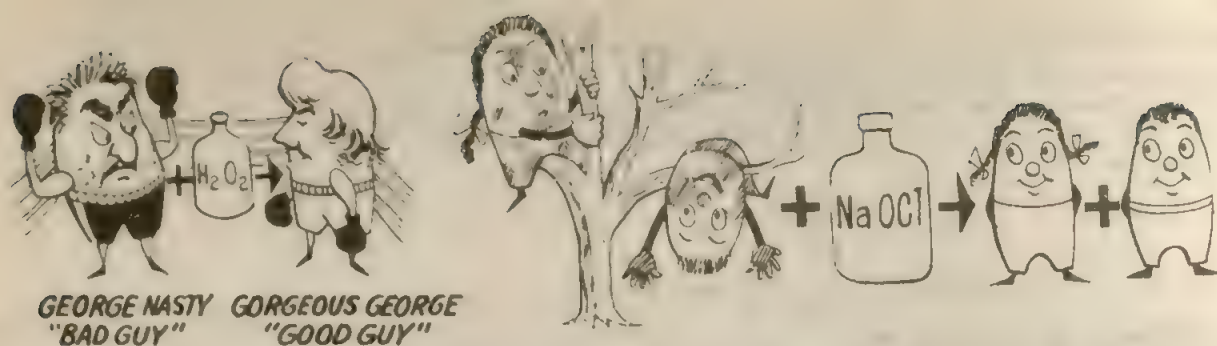


Figure 8.6 Two familiar oxidizing agents and uses thereof.

Sodium hypochlorite (NaOCl), available in aqueous solution as a laundry bleach (*Purex*, *Chlorox*, and the like), finds some use in the irrigation of wounds and for bladder infections. It also is used as a disinfectant, deodorizer, and bleach. Solutions of iodine also are used as antiseptics.

The exact function of these oxidizing agents as antiseptics is unknown. Their action is rather indiscriminate; they attack human cells as well as microorganisms. For many purposes, these simple inorganic compounds have been replaced by organic compounds such as the phenols, which kill by other mechanisms.

Other oxidizing agents are used as disinfectants. Calcium hypochlorite [$\text{Ca}(\text{OCl})_2$], bleaching powder, is used to disinfect clothing and bedding. Chlorine (Cl_2) is used to kill pathogenic (disease-causing) microorganisms in drinking water. Also, waste water usually is treated with chlorine before it is returned to a stream or a lake. Such treatment has been quite effective in preventing the spread of infectious diseases, such as typhoid fever. Use of chlorine in this manner came under criticism in 1974, when it was shown that the chlorine reacted with organic compounds (presumably from industrial wastes) to form toxic chlorinated compounds.

Ozone also has been used to disinfect drinking water. Many European cities, including Paris and Moscow, use ozone to treat their drinking water. Ozone is more expensive than chlorine, but less of it is needed. An added advantage is that ozone kills viruses on which chlorine has little, if any, effect. Tests in Russia have shown ozone to be 100 times as effective as chlorine for killing polio viruses.

Ozone (O_3) acts by transferring its "extra" oxygen to the contaminant. The oxidated contaminants are thought to be less toxic than the chlorinated ones. In addition, ozone imparts no chemical taste to the water. We may well see a shift from chlorine to ozone in the treatment of our drinking water and wastewater.

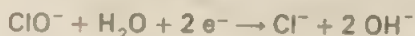
Oxidation: Bleaching and Stain Removal

Bleaches are compounds that are used to remove unwanted color from white fabrics. Nearly any oxidizing agent would do the job. However, some also would harm the fabrics, some would be unsafe, some would produce undesirable by-products, and some would simply be too expensive.

The most familiar laundry bleaches are aqueous solutions of sodium hypochlorite (NaOCl). All the bleaches generally have 4.25% NaOCl , and yet they vary widely in price. Such price variations in standardized products usually result from costly advertising to promote the use of the more familiar brand-name products. Consumers would be wise to read the list of ingredients on the labels of competitive brands and then compare prices.

Bleaching powder [$\text{Ca}(\text{OCl})_2$] generally is preferred for large-scale bleaching operations. The paper industry uses it to make white paper, and the textile industry uses it to make whiter fabrics.

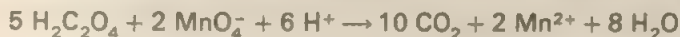
In both aqueous bleaches and bleaching powder, the active agent is the hypochlorite ion, ClO^- . Materials appear colored because loosely bound electrons are boosted to higher energy levels by absorption of visible light. Bleaching agents do their work by removing or tying down these mobile electrons. For example, hypochlorite ions (in water) take up electrons to form chloride ions and hydroxide ions.



Hypochlorite bleaches are safe and effective for cotton and linen fabrics. They should not be used for wool, silk, or nylon.

Other bleaching agents include hydrogen peroxide, sodium perborate (often formulated $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$ to indicate a complex of NaBO_2 and H_2O_2), and a variety of chlorine-containing organic compounds that release Cl_2 in water. When hydrogen peroxide is used to bleach hair, it acts as an oxidizing agent. In the process, the black or brown pigment in the hair (melanin) is oxidized to colorless products.

Stain removal is not nearly so simple a process as bleaching. A few stain removers are oxidizing agents or reducing agents; others have quite different chemical natures. Nearly all stains require rather specific stain removers. Hydrogen peroxide in cold water removes blood stains from cotton and linen fabrics. Potassium permanganate removes most stains from white fabrics (except for rayon). The permanganate stain then can be removed by treatment with oxalic acid.



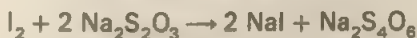
*Oxalic
acid*

(Purple)

(Colorless)

(Oxalic acid also removes rust spots, but its action in that case is as a complexing agent, not a reducing agent. The oxalic acid picks up the otherwise insoluble rust and carries it in a solution that is washed away.)

Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) readily removes iodine stains by reducing iodine to a colorless ion (I^-).



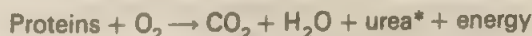
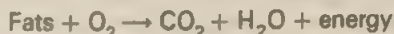
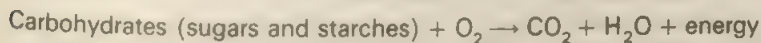
(Brown)

(Colorless)

Many stain removers are simply adsorbants (e.g., cornstarch, which removes grease spots), solvents (e.g., amyl acetate, or acetone, which removes ballpoint ink), or detergents (which remove mustard stains).

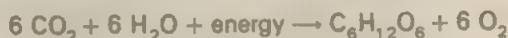
Oxidation, Reduction, and Living Things

Living organisms obtain energy for physical and mental activities by the slow, multistep oxidation of food. These processes are discussed in more detail in later chapters, but for now we can represent them like this.



*In some organisms, the nitrogen winds up as ammonia (NH_3) rather than as urea.

Green plants make these foods by the reduction of carbon dioxide and water, and we eat either the plants or the animals that the plants feed. Energy for the reduction reaction, called *photosynthesis*, comes from the sun. The process, shown here for the formation of glucose (a simple sugar) can be written



This reaction is precisely the reverse of the oxidation reaction given above for carbohydrates if the sugar is glucose.



We can see that green plants provide the reducing agents that make possible all life on Earth. Animals carry out oxidation and so are able to survive only because plants provide the materials that they oxidize. Therefore, we could consider crop farming a process of reduction. Energy captured in cultivated plants, whether the plants are used directly or are fed to animals, is the basis of human life. If plants couldn't reduce, and if we couldn't oxidize, there would be no life.

Problems

- Write formulas for the products formed when each of the following burns (that is, reacts with oxygen).

a. C	c. N ₂	e. CS ₂
b. S	d. CH ₄	f. C ₆ H ₁₂ O ₆
- To test for an iodide ion (for example, in iodized salt), a solution is treated with chlorine to liberate iodine. The reaction is:



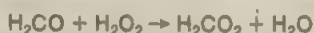
Which substance is oxidized? Which is reduced?

- Molybdenum metal, used in special kinds of steel, can be manufactured by the reaction of its oxide with hydrogen. The reaction is:



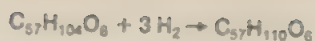
Which substance is reduced? Which is the reducing agent?

- Define *oxidation* and *reduction* in terms of the following processes.
 - Oxygen atoms gained or lost
 - Hydrogen atoms gained or lost
 - Electrons gained or lost
- List four common oxidizing agents.
- List three common reducing agents.
- Describe how a bleaching agent, such as hypochlorite (ClO⁻), works.
- In the reaction



Which substance is oxidized? Which is the oxidizing agent?

- Ethylene, C₂H₄, reacts with hydrogen to form ethane, C₂H₆. Is the ethylene oxidized or reduced? Explain your answer.
- The oxidizing agent that we use to obtain energy from food is oxygen (from the air). If you breathe 15 times a minute (at rest), taking in and exhaling 0.5 L with each breath, what volume of air do you breathe each day? Air is 21% oxygen by volume. What volume of oxygen do you breathe each day?
- To oxidize 1 kg of fat, our bodies require about 2000 L of oxygen. A good diet contains about 80 g of fat per day. What volume of oxygen is required to oxidize that fat?
- Unsaturated vegetable oils react with hydrogen to form saturated fats. A typical reaction is:



Is the unsaturated oil oxidized or reduced? Explain.

- 13 In what sense are humans oxidizing agents and green plants reducing agents?

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chapter 9

Chemistry of the Earth: The Materials Crunch

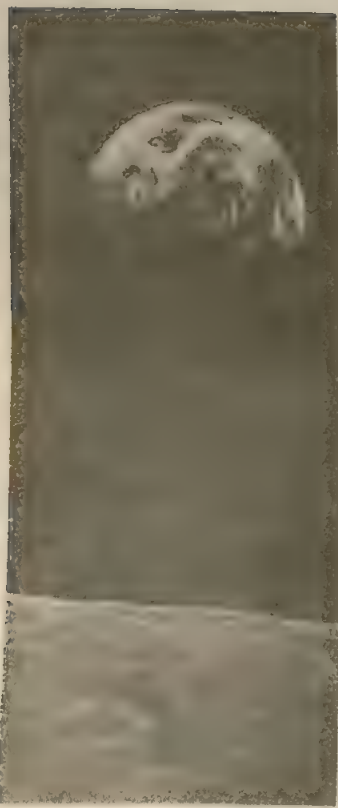


Figure 9.1 Spaceship Earth with the desolate moon in the foreground. (Courtesy of the National Aeronautics and Space Administration.)

This world is indeed wondrous. We have sent astronauts to the barren moon and watched their wanderings on television. We have sent machines to Mars to photograph its utter desolation. We have sent spacecraft to Venus to measure its inhospitably high temperatures. Through these explorations, we have come at last, in these last decades of the twentieth century, to realize that the Earth is a small island of green and blue in the vastness of space. Indeed, some people have begun to look upon the Earth as a spaceship with limited supplies aboard and to call for the judicious use—and reuse—of those supplies.

What sort of materials are we carrying along on Spaceship Earth? Are they sufficient for the 4 billion astronauts aboard? Will they be sufficient for the 7 billion expected to travel upon it by the end of this century? Let's start out to answer these questions by first looking at the elemental composition of the Earth.

Spaceship Earth: What It Is Made Of

Structurally, the Earth is divided into three main regions: the *core*, the *mantle*, and the *crust*. The core is thought to consist largely of iron (Fe) and nickel (Ni). Since it is not accessible, and since it does not seem likely that it will ever become so, we won't consider the core as a source of materials.

The mantle is believed to be composed mostly of silicates—compounds of silicon and oxygen with a variety of metals. Although it is conceivable that the mantle will be reached eventually, it probably has few useful materials that are not available in the more accessible crust.

The crust is the outer shell of the Earth. It has three parts: the *lithosphere* (solid part), the *hydrosphere* (oceans, seas, lakes, rivers, etc.), and the *atmosphere* (air). The lithosphere is about 35 km thick under the continents and only about 10 km thick under the oceans. Extensive sampling of the crust has made it possible for scientists to estimate its elemental composition. Let's consider a random sample of 10 000 atoms from the crust. Of these more than half (5330 atoms) would be oxygen. This element occurs in the atmosphere as molecular oxygen (O_2), in the hydrosphere in combination with hydrogen as water, and in the lithosphere in combination with silicon (pure sand is largely SiO_2) and as various compounds.

The second most abundant element in the Earth's crust is silicon. Of those 10 000 atoms in our sample, 1590 would be silicon. Hydrogen would come in third with 1510 atoms, most of which would be in combination with oxygen in water. Hydrogen is such a light element—the lightest of all—that it makes up only 0.9% of the Earth's crust by weight. Other elements and the number of their atoms in our sample of 10 000 would be: aluminum (Al), 480 atoms; sodium (Na), 180 atoms; iron (Fe) and calcium (Ca), 150 atoms each; magnesium (Mg), 140 atoms; and potassium (K), 100 atoms. These nine elements would account for 96.30 of the atoms, leaving only 370 atoms of all the other elements. These figures are summarized in **table 9.1**.

Table 9.1
Composition of the Earth's surface, atoms of each element
in a sample of 10,000 atoms and percent by weight

<i>Element</i>	<i>Symbol</i>	<i>Number of Atoms</i>	<i>Percentage by Weight</i>
Oxygen	O	5330	49.5
Silicon	Si	1590	25.7
Hydrogen	H	1510	0.9
Aluminum	Al	480	7.5
Sodium	Na	180	2.6
Iron	Fe	150	4.7
Calcium	Ca	150	3.4
Magnesium	Mg	140	1.9
Potassium	K	100	2.4
All others	—	370	1.4
Total		10 000	100.0

There are some very important elements, such as carbon (C), nitrogen (N), and phosphorus (P), in that category of all others. As **table 9.1** indicates, these elements are rather scarce on Spaceship Earth.

Table 9.2
Composition of the Earth's atmosphere (dry),
molecules of each substance per 10 000 molecules

<i>Substance</i>	<i>Formula</i>	<i>Number of Molecules</i>
Nitrogen	N ₂	7800
Oxygen	O ₂	2100
Argon	Ar	93
Carbon dioxide	CO ₂	3
All others	—	4
Total		10 000

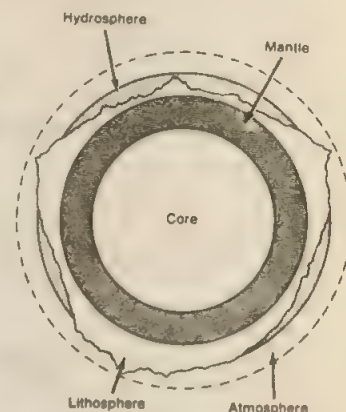


Figure 9.2 Schematic diagram of the Earth (not drawn to scale).

The foregoing analysis applies to the Earth's crust as a whole. Now let's turn our attention to each of the three divisions of that crust.

The Atmosphere: A Thin Blanket of Gases

It is difficult to measure just how deep the atmosphere is. It does not end abruptly but gradually fades as the distance from the surface of the Earth increases. It is known, though, that 99% of the atmosphere lies within 30 km of the surface of the Earth. A thin layer of air indeed—like the peel of an apple, only relatively thinner. Our supply of air, once thought to be inexhaustible, now appears definitely limited.

Air is a mixture of gases. Dry air is (by volume) about 78% nitrogen (N_2), 21% oxygen (O_2), and 1% argon (Ar). Water vapor varies from 0% up to about 4%. There are a number of minor constituents, the most important of which is carbon dioxide (CO_2). The concentration of carbon dioxide in the atmosphere is believed to have increased from 296 ppm in 1900 to its present value of 318 ppm. It's most likely that it will continue to rise as we burn more and more fossil fuels (coal, oil, and gas). The composition of the atmosphere is summarized in table 9.2.

The Nitrogen Cycle

Although nitrogen makes up 78% of the atmosphere, the N_2 molecules can't be used directly by higher plants or by animals. They first have to be fixed—that is, combined with another element.

Certain types of bacteria convert atmospheric nitrogen (N_2) to nitrates. Other bacteria convert the nitrogen in compounds back to N_2 . Thus, a nitrogen cycle (figure 9.3) is established. Lightning also serves to fix nitrogen by causing it to combine with oxygen. Nitric oxide (NO) and nitrogen dioxide (NO_2) are formed. The equations are

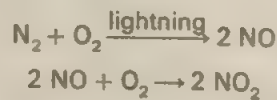
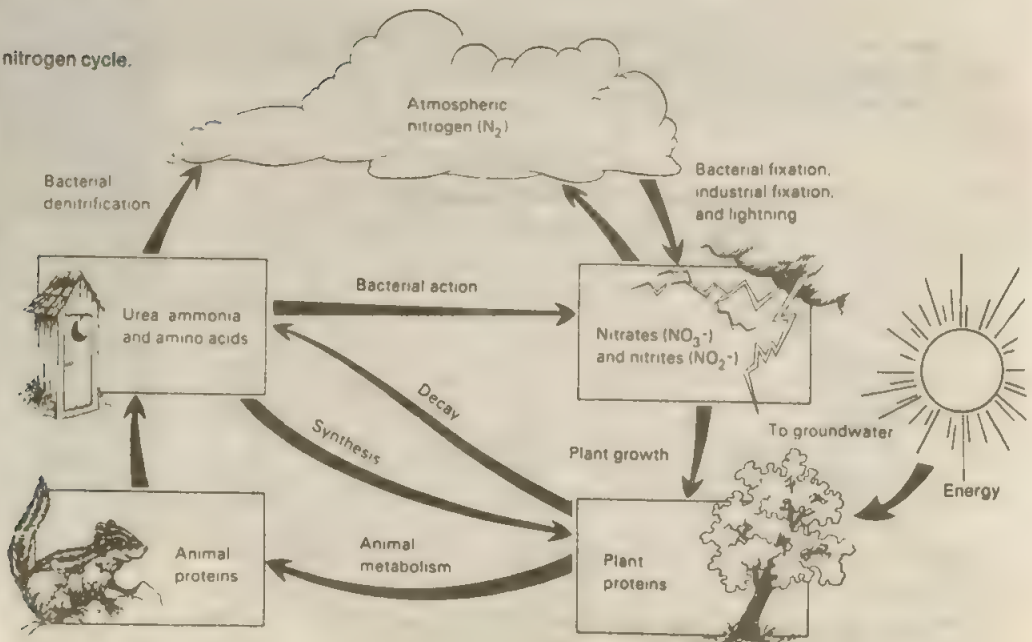


Figure 9.3 The nitrogen cycle.



Nitrogen dioxide reacts with water to form nitric acid (HNO_3).



The nitric acid falls in rainwater, adding to the supply of available nitrates in the oceans and the soil.

Humans have undertaken substantial intervention in the nitrogen cycle by fixing nitrogen industrially in the manufacture of nitrogen fertilizers. This intervention has greatly increased our food supply, since the availability of fixed nitrogen is often the limiting factor in the production of food (chapter 15). Not all the consequences of this intervention have been favorable, however; excessive runoff of nitrogen fertilizer has led to serious water-pollution problems in some areas (chapter 18).

The Oxygen Cycle

The element oxygen makes up 21% of the Earth's atmosphere. The oxygen supply is constantly being replenished by green plants, including one-celled organisms called phytoplankton in the sea. Oxygen is used by both plants and animals in the metabolism of foods. It also is used in the decay and the combustion of plant and animal materials. Some oxygen is consumed in the rusting of metals and in the weathering of rocks. A simplified oxygen cycle is illustrated in figure 9.4.

In the upper atmosphere, some oxygen is formed by the action of ultraviolet rays on water. Perhaps more important, some oxygen is converted to ozone.



The ozone, in turn, absorbs short-wavelength ultraviolet radiation that would otherwise make any sort of life on Earth close to impossible.

We discuss the atmosphere in more detail in chapter 19 and pay particular attention to the changes wrought by human activities.

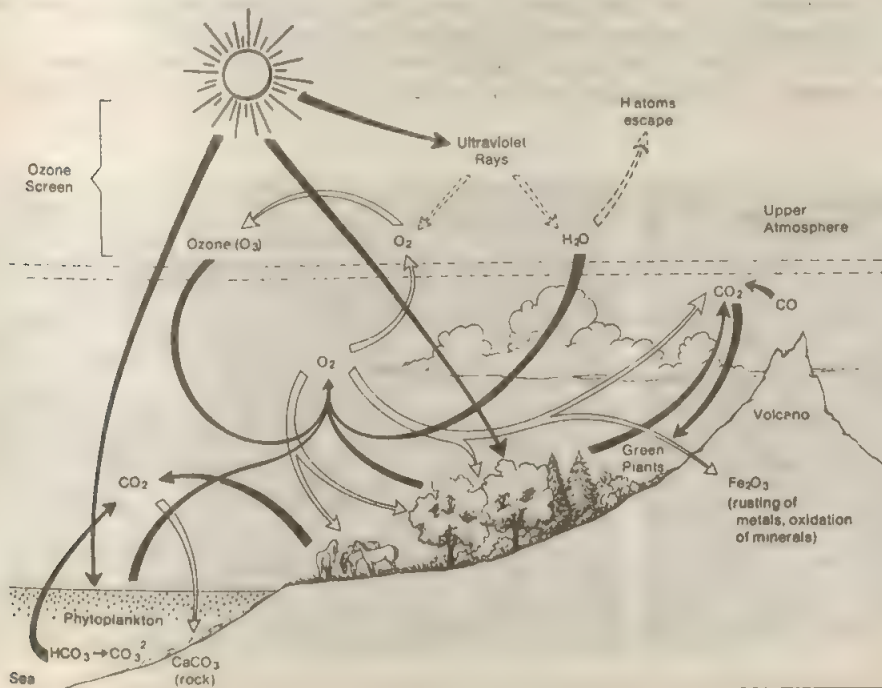


Figure 9.4 The oxygen cycle.

The Hydrosphere: Water

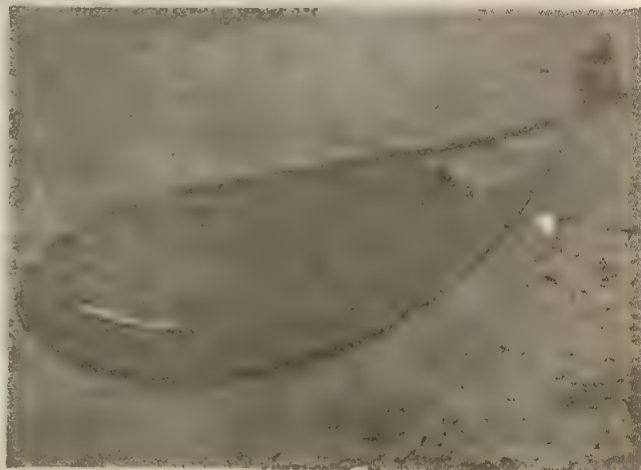
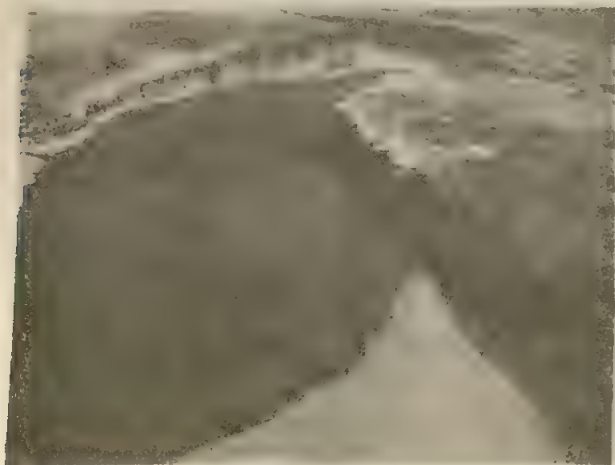
Next to air, water is the most familiar substance on Earth. Even so, it is a most unusual compound. It is the only common liquid on the surface of our planet. The solid form of water (ice) is less dense than the liquid. The consequences of this peculiar characteristic are immense for life on this planet. Ice forms on the surface of lakes and insulates the lower layers of water. This enables fish and other aquatic organisms to survive winters in the temperate zones. If ice were more dense than liquid water, it would sink to the bottom as it formed and even the deeper lakes of the northern United States would freeze solid in winter. Life in the northern lakes and rivers would be very different from what it now is, if indeed there were life in those waters at all.

The same property—ice less dense than liquid water—has dangerous consequences for living cells. As ice crystals are formed, the expansion ruptures and kills the cells. The slower the cooling, the larger the crystals of ice and the more damage there is to the cell. Frozen food manufacturers take advantage of the properties of water when they freeze foods so rapidly that the ice crystals are kept very small and do minimum damage to the cellular structure of the food; the industry calls such foods “flash frozen.” The possibility of preserving people’s bodies for resurrection in some future age would depend on freezing the body quickly enough to prevent the destruction of cells. Perhaps you have heard of plans to preserve the body of a person who dies of cancer and then revive it after a cure for cancer has been found. This would require freezing the body almost instantly after death. The freezing portion of the scheme has been carried out on a number of bodies. To date no revivals have been successful.

Another unusual property of water is its high heat capacity. It takes almost 10 times as much heat to raise the temperature of 1 g of water by 1 °C as it takes to raise the temperature of 1 g of iron by the same amount. Conversely, much heat is given off by water for even a small drop in temperature. The vast amounts of water on the surface of the Earth thus act as a giant thermostat to moderate the daily temperature variations. You need only consider the extreme temperature changes on the surface of the waterless moon to appreciate this important property of water.

Water also has a higher density than most other familiar liquids. As a consequence, those liquids that are less dense than water and are also insoluble in

Figure 9.5 Oil is insoluble in, and less dense than, water, so oil spills float on the surface of the bodies of water affected by the oil spills. The left photo shows crude oil and debris on the San Juan River. A portion of the spill has been enclosed in a boom (right) and is being towed ashore for pickup. (Courtesy of the United States Environmental Protection Agency.)

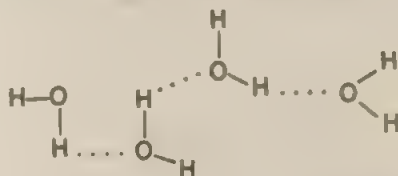


water float on the surface of it. A familiar problem in recent years has been the gigantic oil spills that occur when a tanker ruptures or when an offshore well gets out of control. The oil, floating on the surface of the water, often is washed onto beaches, where it does considerable ecological and aesthetic damage. If water were less dense than oil, the problem would certainly be of a different nature, though not necessarily less acute.

Still another way in which water is unique is that it has a very high heat of vaporization; that is, a large amount of heat is required to evaporate a small amount of water. This is of enormous importance to living animals in that large amounts of body heat can be dissipated by the evaporation of small amounts of water (perspiration) from the skin. This effect also accounts for the climate-modifying property of lakes and oceans. A large portion of the heat that could otherwise heat up the land is used instead to vaporize water from the surface of the lake or the sea. Thus, in summer it is cooler near a large body of water than in interior land areas.

The Structure of Water

All these fascinating properties of water depend on the unique structure of the water molecule (chapter 5). Recall that the water molecule is polar (**figure 9.6**). In the liquid state, water molecules are strongly associated by the attraction of the positive end of one molecule for the negative end of another. This can be represented schematically as:



This association is random, however, and the molecules are fairly close together. When water freezes, the molecules take on a much more ordered arrangement with large, hexagonal holes (**figure 9.7**). This structure extends on out in all directions for billions of atoms. The large holes account for the fact that ice is less dense than liquid water.

The Salt of the Sea

Because of its polar nature, water tends to dissolve ionic substances (chapter 5). The oxygen ends (negative) of the water molecules (in **figure 9.8**, the shaded circles represent the oxygen and the smaller circles represent the hydrogen) are pointed toward the positive ion and the hydrogen ends (positive) are pointed toward the negative ion.

This solvent power of water accounts for the saltiness of the sea. Rainwater dissolves minerals (ionic in nature), and these are carried by streams and rivers to the sea. There the heat of the sun evaporates part of the water, leaving the "salts" behind. The oceans grow more salty as the years go by, but this is a very slow process, and the increase in salt content would not be noticeable in one lifetime.*

*At the present rate of salt accumulation, the seas would become saturated with salt (about 36%) in another 3.5 billion years. If our descendants are still around in that distant age, they will find our oceans much like today's Dead Sea.

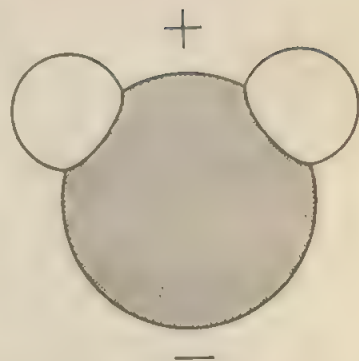


Figure 9.6 A model of a water molecule, which indicates water's polar nature.

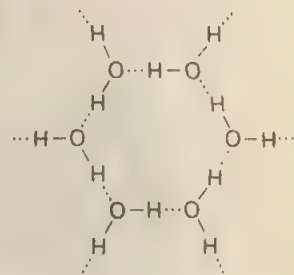


Figure 9.7 The structure of ice.

Water, Water, Everywhere

Three-quarters of the surface of the Earth is covered with water. About 20 sextillion L (20 000 000 000 000 000 000, or 2×10^{22} , L) of rainwater fall upon the Earth each year. That is indeed a lot of water. Nearly 98% of the water on Earth, though, is sea water—unfit for drinking and not even suitable for most industrial purposes. Much of the rainwater falls into the sea or on areas otherwise inaccessible. Something less than 2% of the water is frozen in the polar ice caps, leaving less than 1% (about 300 quadrillion L) available as fresh water. The average use of water per person (including that used for industrial, agricultural, and other purposes) in the United States is 2 million gal per year. At this rate of use (and assuming complete recycling each year), the water supply on Earth could support a population of 40 billion people. But the rate of use is increasing rapidly, and the water is not always where the people are. Quite often, too, freshwater supplies are so badly polluted that they are unfit for human use.

The Water Cycle

The distribution of water between the sea, the ice caps, and freshwater rivers, lakes, and streams is fairly constant. There is, however, a dynamic cycle (figure 9.9) of water between these various components. Water is constantly evaporating from both water and land surfaces. This water vapor condenses into clouds and returns to Earth in the form of rain, sleet, and snow. This fresh water becomes part of the ice caps, runs off in streams and rivers, and fills lakes and underground reservoirs.

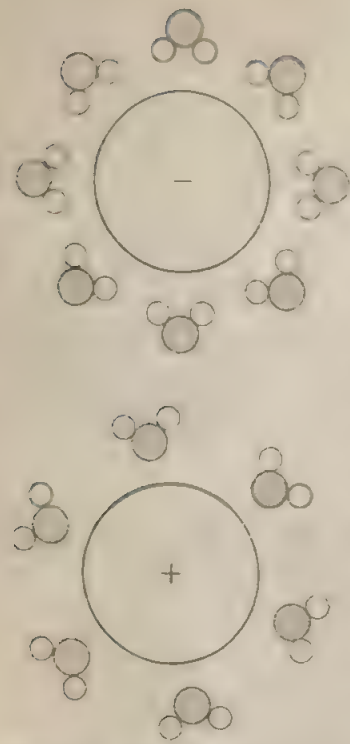
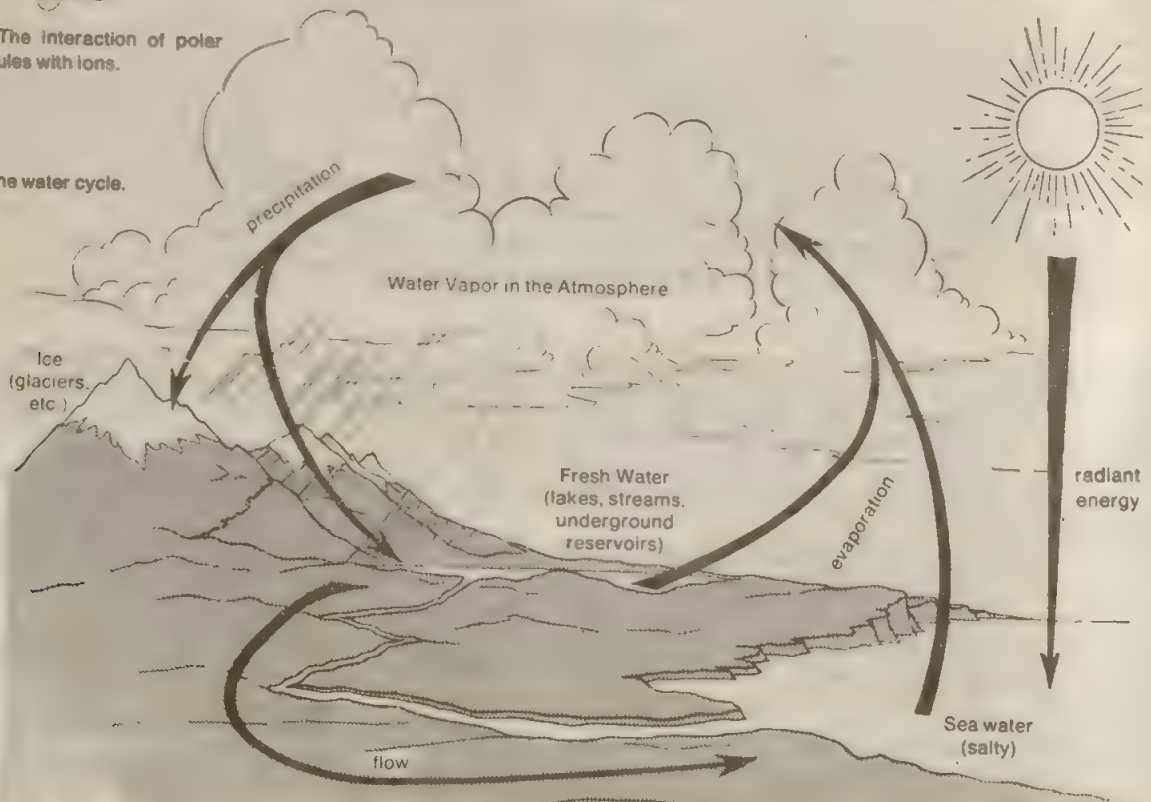


Figure 9.8 The interaction of polar water molecules with ions.

Figure 9.9 The water cycle.



This cycling of water serves to replenish our supply of fresh water. When water evaporates from the sea, the salts are left behind. When water moves through the ground, impurities are trapped in the rock, gravel, sand, and clay. This capacity to purify is not infinite, however, as we see in chapter 18, where we look at the effect of humans on the hydrosphere.

The Lithosphere: Organic and Inorganic

Rocks and minerals make up the greater part of the lithosphere. Prominent among these are *silicates* (compounds of metals with silicon and oxygen), *carbonates* (metals combined with carbon and oxygen), and *sulfides* (metals combined with sulfur only). There are thousands of these mineral compounds making up the *inorganic* portion of the solid crust.

Though much, much smaller in quantity, the *organic** portion of the lithosphere includes all living creatures, their waste and decomposition products, and fossilized materials such as coal, natural gas, petroleum, and oil shale that once were living organisms. This organic material *always* contains the element carbon, nearly always also has combined hydrogen, and often contains oxygen, nitrogen, and a variety of other elements.

We devote several later chapters to organic materials, but for the remainder of this chapter, let's concentrate on the inorganic portion of the lithosphere.

Meeting Our Needs and Wants: Chemical Change

The needs of primitive people were few. Food was obtained by hunting and gathering. Clothing, when it was needed, was provided by the skins of animals. Shelter was found in a convenient cave or constructed from readily available sticks and stones and mud. At this level of subsistence, though, the Earth could support only a few million people.

After the agricultural revolution (about 10 000 B.C.), people no longer were forced to search for food. Domesticated animals and plants supplied their needs for food and clothing. A reasonably assured food supply enabled them to live in cities. City life created a demand for more sophisticated building materials. People learned to convert natural materials to products with superior properties. Clay, a complex mixture of silicates, makes a building material far superior to adobe (sun-dried bricks) after being formed into bricks and heated to high temperature. A similar process was used to make pottery. These ceramic objects made the preparation and storage of food a lot easier.

People also learned quite early to improve the foods provided by nature. Fire was one of the earliest agents of chemical change. Cooking meat and grains improved their flavor and probably made their digestion easier. People also found ways to convert fruits and starchy grains into alcoholic beverages. This chemical change, we now know, is brought about by single-celled organisms called yeast. We also know that the process involves the conversion of a simple sugar, such as glucose, into ethyl alcohol and carbon dioxide.

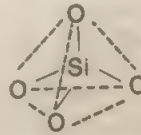


*That branch of science called *organic chemistry* was once simply the study of compounds found in the life-based portion of the lithosphere. With the advent of many synthetic chemicals with similar properties, the definition has been broadened and can be simply stated as the study of the compounds of carbon. The chemistry of all the other elements and their compounds is called *inorganic chemistry*.

The domestication of plants and animals and the ability to manipulate natural materials made it possible for the Earth to support a substantially larger population than it had in the hunting and gathering age.

Silicates and the Shape of Things

There are thousands of different minerals in the lithosphere. We can consider only a few representative ones here. First, let's look at some of the silicates. The basic unit of silicate structure is the SiO_4 tetrahedron.



Silicate tetrahedra can be arranged in a linear manner to form fibers (asbestos), in planar sheets (mica), and in complex three-dimensional arrays (quartz, feldspar).

Pure quartz is composed of silicon and oxygen only. Although the basic unit of quartz is the SiO_4 tetrahedron, the ratio of atoms is only 1:2, since *all* oxygen atoms are shared by adjacent tetrahedra (figure 9.10). Thus, the simplest formula for quartz is SiO_2 .

The micas are composed of SiO_4 tetrahedra arranged in a two-dimensional, sheetlike array. Mica is easily cleaved into thin, transparent sheets. Large pieces of mica sometimes were used as windows before glass became generally available. Figure 9.11 includes a photograph of mica and a diagram of its chemical structure.

Asbestos is a generic term for a variety of fibrous silicates. Perhaps the best known of these is chrysotile, a magnesium silicate. A sample of this mineral is shown in figure 9.12. Note that the chrysotile is a double chain of SiO_4 tetrahedra. The oxygen atoms that have only one covalent bond also bear a negative charge. It is with these that the magnesium ions (Mg^{2+}) are associated.

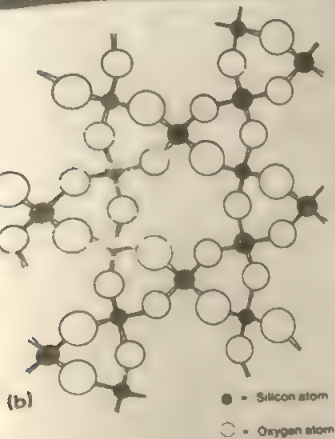


Figure 9.10 (a) A sample of quartz crystals. (Courtesy of Ward's Natural Science Establishment, Inc.) (b) The chemical structure of quartz.

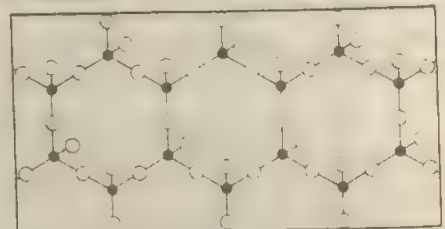
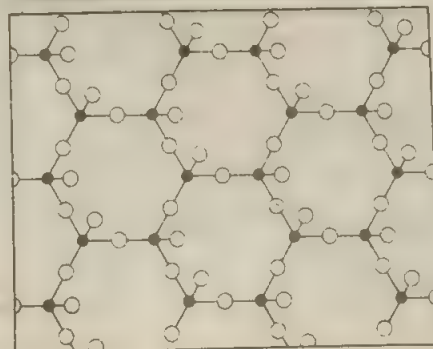
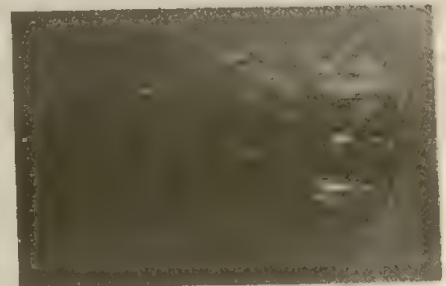


Figure 9.12 (a) A sample of chrysotile. (Photo by Dennis Tasa.) (b) The chemical structure of chrysotile.

Asbestos has been used widely. It is an excellent thermal insulator. Great quantities of it have been used to insulate furnaces, heating ducts, and steam pipes. It is used to make protective clothing for firefighters and others who are exposed to flames and high temperatures. It is used in brake linings for automobiles. Asbestos filters have been used in the preparation of foods and beverages. Small amounts of the fibers have been found in beer, wine, and soft drinks. Asbestos also has been found in several brands of talcum powder. (This is not particularly surprising, talc is also a silicate mineral, and talc stone often is contaminated with asbestos.)

Perhaps the most notable case of asbestos pollution has occurred in and around Lake Superior. Several cities take their drinking water from the lake. The water was found to contain low levels of asbestos fibers. The pollution was traced to a taconite-processing plant at Silver Bay, Minnesota. (Taconite is a low-grade iron ore.) Eventually, the plant was ordered to dispose of its asbestos-contaminated tailings on land, rather than dumping them into the lake. It will probably be many years, though, before the asbestos is gone from the waters of the lake.

The health hazards to those who work with asbestos are well known. The tiny, almost indestructible fibers readily penetrate the tissues of the lungs and the digestive tract. Over a period of 10 to 20 years, inhalation of fibers 5 to 50 μm long causes *asbestosis*, a severe respiratory disease. After 30 to 45 years, some workers contract lung cancer and others, mesothelioma, a rare and incurable cancer of the linings of various body cavities.

Asbestos workers who also smoke cigarettes run a much greater risk of getting cancer than those who don't. They also face a greater risk than those who smoke but don't work with asbestos. Cigarette smoke and asbestos fibers work together to produce an effect much greater than just the sum of the expected effects. Such an interaction is called a *synergistic effect*.

Occupational exposure to asbestos fibers can be devastating to workers. Indeed, the United States Environmental Protection Agency has banned the use of asbestos in spray-on fireproofing in building construction. But what about the general public? Generally, we are exposed to much lower levels than are those who work with asbestos. The effects of exposure to small quantities of asbestos are unknown. The risk for the general public is probably quite small, but there is some risk. And, if we want to take advantage of the remarkable properties of asbestos, we have to assume some risk.

Modified Silicates: Glass, Ceramics, and Cement

Sand, mica, and asbestos are used much as they occur in nature. Some disruption of nature is necessary when the materials are mined; some environmental hazard is encountered in their use and disposal. However, little expenditure of energy is necessary, and no new materials are introduced into the ecosystem.

People long have been able to modify nature's materials to more nearly satisfy their needs and wants. For centuries, the technological developments were based largely on trial and error. Modern science has, by developing an understanding of the structure of materials, greatly increased the human capacity for the modification of natural materials. Thus, technological advances have been greatly accelerated by scientific knowledge.

One of the earliest technologies to develop was that used in the manufacture of pottery. Early potters used natural clays, which they merely hardened by heat. Clays are exceedingly complex, and their composition varies widely, but they are basically aluminum silicates formed by the weathering of more complex silicates such as feldspar. When clay is mixed with water, it can be molded into any shape. Firing leaves a hard, resistant but porous product. Bricks and tile are made in this manner.



Figure 9.13 Protective clothing made of asbestos is worn routinely by workers in many American industries. (Courtesy of Asbestos Information Association of North America.)

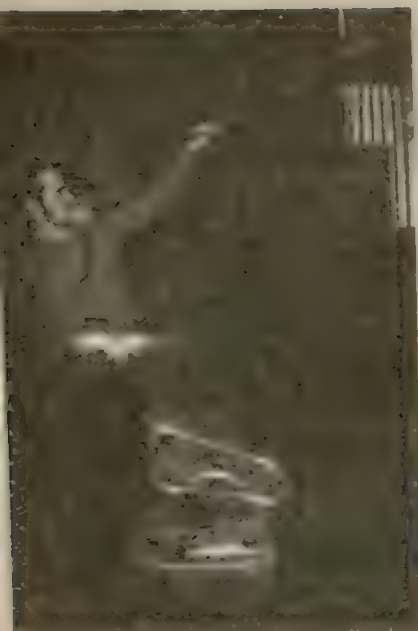


Figure 9.14 Glassblowing. (Courtesy of the Rocky Mountain Glass Company, Durango, Colo.)

When porosity is not desirable—as in a cooking pot or a water jug—the pottery can be glazed by adding various salts to the surface. Heat then converts the entire surface to a glasslike matrix.

A study of the structure and properties of clays and glazes has led to the development of fantastic new ceramic materials—from those that withstand the extreme temperatures of rocket exhaust nozzles to magnetic ceramics that serve as memory elements in computers.

Glass is another technological development of ancient times. The first glass probably was made in ancient Egypt about 5000 years ago by heating a mixture of sand, sodium carbonate (Na_2CO_3), and limestone (calcium carbonate, CaCO_3). As the mixture melts, it becomes a homogeneous liquid. When the liquid cools, it becomes a hard, transparent material.

When crystalline materials are heated, they eventually melt over a narrow temperature range. Glass is different; when heated, it gradually softens. While soft, it can be blown, rolled, pressed, and molded into almost any shape. The properties of glass are interpreted in terms of an irregular arrangement, in three dimensions, of SiO_4 tetrahedra. The chemical bonds in this arrangement are not all equivalent, as they are in a crystalline substance. Thus, when glass is heated, the weaker bonds break first and the glass gradually softens.

The basic ingredients in glass can be used in widely varied proportions. Oxides of various metals can be substituted in whole or in part for the lime, soda, or sand. Thus, a wide variety of special glasses can be made. Some examples are given in table 9.3.

Table 9.3
Composition and properties of glasses

Type	Composition	Special Properties
Ordinary glass (soft glass, soda-lime glass)	Sodium and calcium silicates	Soft, with low melting point
Flint glass (optical glass)	Lead oxide (instead of lime)	Highly refractive
Borosilicate glass (<i>Pyrex</i> , <i>Kimax</i>)	Boron oxide instead of some of the silica	Heat resistant
Glass in red signal lights	Selenium and zinc oxide (in addition to silica)	Red, transparent
Glass in ultraviolet lights	Nickel oxide (in addition to silica)	Transparent to ultraviolet rays, opaque to visible light

No vital raw materials are used in the manufacture of ordinary glass, but a good deal of energy—a gas or an oil furnace usually is used—is required to melt and shape glass. Disposal presents a problem, since glass is one of the most permanent materials known. It doesn't rot when discarded.

Cement is still another ancient technological development. The Romans used

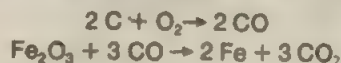
cement to construct roads, aqueducts, and the famous Roman baths. The raw materials for the production of cement are limestone (calcium carbonate, CaCO_3) and clay (aluminum silicates). The materials are finely ground, mixed, and roasted at about 1500°C (in a kiln heated by burning natural gas or powdered coal). The finished product is mixed with sand and gravel to form concrete.

Our understanding of the complex chemistry of cement is still imperfect. Nevertheless, several varieties of cement with special properties are available. There is a cement that sets quickly, with high early strength; a white cement; a waterproof cement; one that sets at high temperatures; and many other varieties.

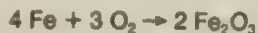
The production of cement involves extensive mining, with whole mountains being torn down for limestone rocks. The rotary kiln process consumes large quantities of irreplaceable fossil fuels. Particulate matter from the crushing operations and smoke and sulfur dioxide from the burning of fossil fuels make air pollution from cement plants especially serious. In use, concrete covers what once were green acres. In cities, the amount of paving with concrete and asphalt is enough to change the climate (temperature and rainfall). Runoff of rainfall from paved areas is especially rapid and contributes to flash flooding. But cement itself doesn't seem to be a bad pollutant. It can be broken up and used as a rock fill.

Metals and Ores: The Iron Age Lives!

Human progress through the ages often is described in terms of the materials that were used for making tools. Thus, we speak of the stone age, the bronze age, and the iron age. Over 2000 years ago, artisans learned to reduce certain metal ores to free metals. For iron, carbon (charcoal) was employed as the reducing agent.



The iron can be softened by heating and then shaped into useful items. These items slowly rust; that is, they are oxidized by oxygen in the air.



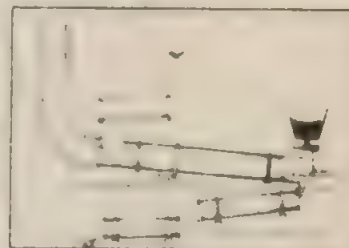
Thus, a cycle is established by which a metal is obtained from its ore and then slowly is corroded back to the combined state (figure 9.16). This rust could be reduced back to metal and reused, but this is seldom done. The rust often is scattered in the environment and, for all practical purposes, lost. Many metal objects are melted down, the rust removed or reduced, and new objects molded from the molten metal. But a lot of metal is still discarded in dumps. As we use up high grade ores, we may have to start mining the dumps for metals.

For many purposes, iron has been replaced by other metals and plastics. Our age has been given many names—the age of plastics, the nuclear age, and the computer age. Each name is appropriate in its own way. As far as the use of materials is concerned, however, we are still in the midst of the iron age. We use far more iron than any other metal for making tools and machines (table 7.4).

Pure iron is too soft and reactive to be useful for most purposes. Most iron is converted to *steel* by adjusting the carbon content. The properties of steel can be adjusted over a wide range, depending on the amount of carbon in it. High-carbon steel is hard and strong. Low-carbon steel is ductile (can be drawn into wire) and malleable, and it can be forged and welded. Some steel is alloyed with other metals and has still other properties. (An *alloy* is a mixture of two or more elements, at least one of which is a metal. The alloy has metallic properties.) Iron, because it can be formed into steel and so many other alloys, is the most useful of all the metals.



(a)



(b)

Figure 9.15 (a) A cement kiln. (b) A diagram of a cement kiln. (Courtesy of Huron Portland Cement Company.)

Figure 9.16 The metal cycle.

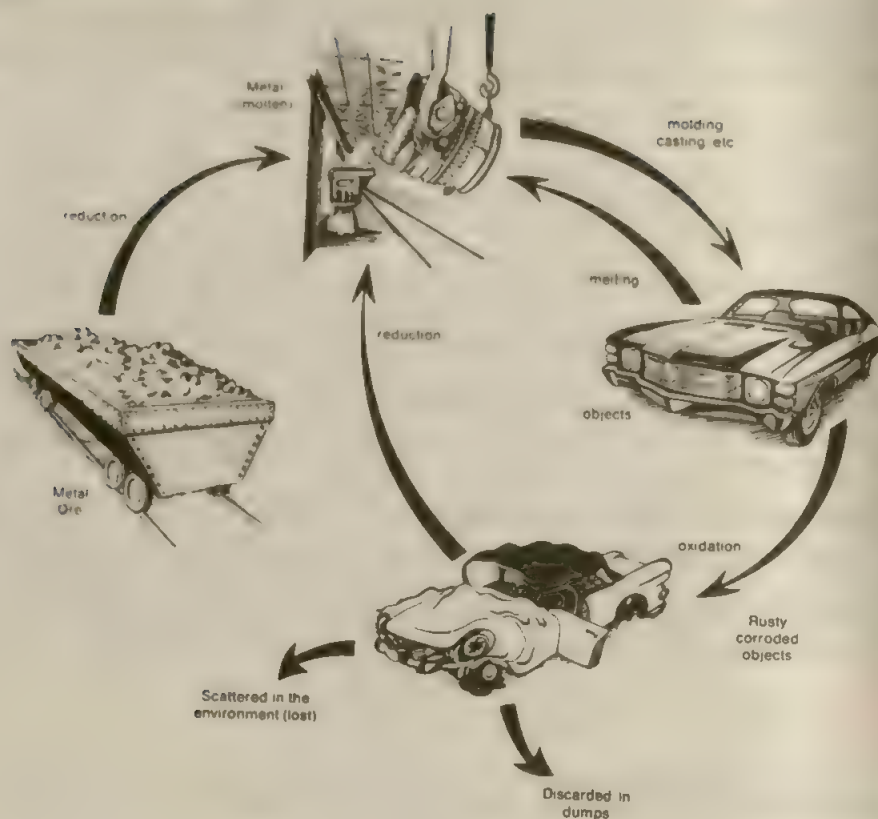


Table 9.4
United States and world production of several metals and ores
in metric tons* for 1974

Metal or Ore	United States	World
Iron (Fe)	51 125 000	507 500 000
Bauxite ($\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$)	2 408 000	78 200 000
Magnesite (MgCO_3)	—	11 810 000
Manganese (Mn)	31 600	9 530 000
Copper (Cu)	1 448 800	7 630 000
Zinc (Zn)	453 500	555 000
Lead (Pb)	602 300	3 430 000
Chromium Oxide (Cr_2O_3)	—	3 310 000
Nickel (Ni)	15 868	750 500
Tin (Sn)	72	180 500
Mercury (Hg)	75	9 240
Silver (Ag)	1 050	9 230

Chapter Nine Data from Department of Economic and Social Affairs, *Statistical Yearbook 1975*, New York: United Nations, 1976.

120 *A metric ton (t) is 1000 kg, or about 2204 lb.

In recent years, iron has been replaced by aluminum for many purposes. Aluminum is the most abundant metal in the Earth's crust, but it is tightly bound in its compounds in nature. Much energy is required to extract aluminum metal from its ores. The principal ore of aluminum is bauxite, a mineral in which aluminum oxide is associated with one, two, or three water molecules per Al_2O_3 unit. The formula for bauxite often is written $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. The bauxite also contains iron oxides, silicates, and other impurities. It is extracted with a strong base and then heated to form the oxide, Al_2O_3 . The oxide is melted and separated by passing electricity through it.



Aluminum is light and strong. It corrodes much more slowly than iron, and, for many purposes, that is a considerable advantage. For one familiar use, though, slow corrosion is a distinct disadvantage. Consider the lowly beverage container. A tin can—really steel with a thin coating of tin on the outside—rusts when thrown away, eventually disappearing. An aluminum can degrades much more slowly. Scientists at Pennsylvania State University estimate that it would take 500 years for one to be completely degraded.

Both steel mills and aluminum plants create considerable pollution. Steel mills discharge lime, acids, grease and oil, and iron salts into the water. They also discharge particulate matter, carbon monoxide, nitrogen oxides, and other air pollutants. The manufacture of aluminum results in the discharge of iron, aluminum, and other metal oxides into waterways and the release of particulate matter, fluorides, and other pollutants into the air.

Steel and aluminum play vital roles in the modern industrial world. Their economic value cannot be overemphasized. But shouldn't we include the *environmental cost* of producing, using, and discarding these materials?

One further comparison of steel and aluminum: Barry Commoner (see reference 8) estimates that it takes 15 times as much fuel energy to produce aluminum as it does to produce a comparable weight of steel. Aluminum is a lighter (less dense) metal than steel, but making an aluminum can requires 6.3 times as much energy as making a steel can.

We could not attempt to discuss the chemistry of all the metals here. We do, however, encounter a number of other metals, particularly those that cause environmental problems, in later chapters.

Running Out of Everything: The Materials Crunch

Perhaps a less dramatic problem than our energy problem, our shortage of materials is just as serious. When the Europeans first came to North America, the native Americans were mining nearly pure copper in Michigan. Now we mine ore with 0.5% or less copper content. For much of the nineteenth century, we mined high-grade iron ore from the Mesabi Range in Minnesota. Now we mine taconite, a hard rock with small amounts of iron oxide dispersed through it. The same is true for gold and silver; the glory holes of western North America are gone. Indeed, there are few high-grade deposits of any metal ores left that are readily accessible to the industrialized nations.

What's wrong with low-grade ores? Considerable energy is required to concentrate them, and energy costs money. Let's consider an analogy. A bag of popcorn is useful. You could pop it and eat it. The same popcorn, scattered all over your room, would be less useful. Oh, you could gather it all up and then pop it, but that would take a lot of energy. Perhaps more energy than you would care to put into it. Perhaps more energy than you would get back if you popped the corn and ate it.

So we are running out of metals. But aren't atoms conserved? Yes, there are about the same number of iron atoms today as there were 100 years ago. But, through use, we scatter the metals. Getting them back together requires energy, just as getting metals from low-grade ores takes energy.

Metals and other materials are a vital part of the economy. The United States has become increasingly dependent on other nations. Figure 9.17 shows the relative amounts of several materials that the United States imports. Obviously, we are as vulnerable to materials embargoes as we are to oil embargoes.

Table 9.5
Estimated year of exhaustion of reserves
of metals, assuming future consumption at
the present rate

Element	Year
Al	2145
Cr	2550
Co	2125
Cu	2010
Au	1990
Fe	2400
Pb	1990
Mn	2150
Hg	1985
Mo	2070
Ni	2110
Pt	1995
Ag	1990
Sn	1995
W	2015
Zn	1990

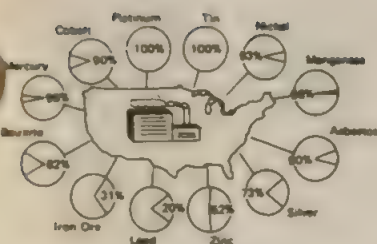


Figure 9.17 The United States imports large portions (those shaded) of 12 essential raw materials (data are for 1973). (From the Statistics and Reports Division of the Agency for International Development, Washington, D.C.)

Adapted from "Chem I Supplement: Emphasis on Elements," *Journal of Chemical Education*, September 1977, p. 551.

Where will we get metals in the future? The sea is one possible source. Nodules rich in manganese cover vast areas of the ocean floor. These nodules also contain copper, nickel, and cobalt. Questions of who owns them and how to mine them without major environmental disruption remain to be resolved.

Lousing Up the Lithosphere: Land Pollution

Productivity and creativity have enabled people in industrialized nations to have a fantastic variety of consumer goods in enormous quantities. As these are broken, worn out, or merely become obsolete, their disposal becomes a major problem. The average person in the United States produces 2.5 kg of trash each day. This leads to monumental problems of collection and disposal, costing about \$7 billion each year.

In the past, most solid wastes were simply discarded in *open dumps*. This led to infestation by rats, flies, and other pests that often spread to nearby areas. Open burning led to monstrously offensive air pollution. These open dumps are being rapidly phased out, but they still account for a large proportion of the total land pollution.

Another method of disposal of solid waste is *incineration*. Provided that this is

carried out in properly designed incinerators, air pollution is minimal. A disadvantage is that noncombustibles—metal cans and glass bottles make up a large part of these—must be separated before or after burning. Some cities have used the heat from combustible solid wastes to generate power. The metal and glass components are separated out for recycling. Certainly that is the way to go.

Another method of disposal is the *sanitary land fill*. Garbage and trash is piled into a trench, compacted, and covered over. This eliminates the problem of rats, flies, and odors. But land for such purposes is scarce where it is most needed, near large cities.

Research in the disposal of solid wastes—and in making useful materials from rubbish—is underway and beginning to produce promising results. In Japan, a method for compacting garbage and coating it with asphalt promises to become a source of badly needed building materials. The United States Bureau of Mines has a method for converting garbage to oil, with a yield of about 250 kg from 1000 kg of garbage. Ground-up rubber tires have been found to accelerate plant growth. Waste glass and rubber have been used in road construction. Yet much remains to be done.

We discuss other land-pollution problems, such as pesticides and herbicides, and special problems in the disposal of waste plastics in later chapters.

Recycling: A Way to Save Materials and Energy

One way to postpone the coming shortage of materials is to recycle them. Recycling is not a perfect solution, for in any such process energy is required and some material is unavoidably lost. But recycling does save materials. Over 50% of the copper and lead produced each year comes from recycled materials. About 33% of the iron and steel and 20% of the aluminum also are salvaged. In the future, as raw materials become scarcer, these proportions are bound to rise.

Recycling also saves energy. It takes only 5% as much energy to make new aluminum cans from old ones as it does to make them from aluminum ore. Using a ton of scrap to make new iron and steel saves 1.5 t of iron ore and 0.3 t of coal. It also results in a 74% saving in energy, an 86% reduction in air pollution, and a 76% reduction in water pollution. Let's hear it for scrap!

Reuse: A Better Way

Recycling is obviously a good thing. It isn't necessarily the *best* thing, though. The best thing is *reuse*. Make the item durable enough to withstand repeated use rather than design it for a single use after which it is to be discarded. Consider the lowly beverage bottle. It takes about 6300 J (1500 kcal) of energy to make a nonreturnable half-liter bottle. It takes a little more energy, 8300 J (2000 kcal), to make a more durable, returnable bottle of the same capacity. The returnable bottle is used an average of 12.5 times before it is broken. That is about 660 J per use, only about 10% of the energy used to make the nonreturnable bottle for its single use.

We could recycle the nonreturnable bottle. Recall, though, that glass is made from common materials—lime, soda, and sand. No vital material is saved. Recycling does save energy compared to making glass from raw materials, but it is much *less* efficient than reusing returnable bottles. We can save both materials and energy by making durable items and reusing them as much as possible. Where reuse is not possible, materials should be recycled to the fullest extent.

Problems

1. Which components of the air are fairly constant in concentration? Which vary in concentration? Why?
2. Nitrogen from the atmosphere is fixed through several different industrial processes to make fertilizers. What effect(s) might this fixing have on the nitrogen cycle?

- 3 List three important properties of water.
- 4 Explain why metals can be recycled fairly easily. What factors limit the recycling of metals?
- 5 Why does quartz occur as three-dimensional crystals? Why does mica occur in sheets? Why does asbestos occur as fibers?
- 6 How does the structure of glass differ from that of crystalline silicates? How do the properties of glass differ from those of crystalline substances?
- 7 Why does water expand when it freezes?
- 8 By what chemical process is a metal obtained from its ore?
- 9 By what chemical process does a metal corrode?
- 10 Which is the most abundant element in the Earth's crust? Which is the second most abundant?
- 11 Which is the most abundant metal in the Earth's crust? Why is it not also the most widely used metal? Which is the most widely used metal?
- 12 List three methods of solid-waste disposal. Give the advantages and the disadvantages of each.

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chapter 10

Carbon and Hydrocarbons: A Storehouse of Energy

Energy to sustain life comes ultimately from the sun. On Earth that energy is stored for the most part in carbon and its compounds. Only a small fraction of the sun's energy is captured by green plants and used by them to convert carbon dioxide, water, and minerals into plant tissue, which humans use for food and structural materials. Through the geological ages, a small fraction of such carbon compounds has been buried in the Earth and converted to coal, petroleum, and natural gas. These fossil fuels provide over 90% of the energy to power our modern industrial society.

In this chapter, we look at the element carbon and those of its compounds called *hydrocarbons*. Coal is essentially carbon; petroleum and natural gas are complex mixtures of hydrocarbons. Read on and learn something of the chemical basis of our age and of why it may be such a brief moment in comparison to the billions of years in geologic time.

Coal: The Carbon Rock of Ages

Coal is a complex material. It is composed principally of carbon, but it also contains smaller percentages of other elements. The quality of coal as an energy source is based on its carbon content; the rankings run from low-grade peat and lignite to high-grade anthracite (**table 10.1**). Soft (bituminous) coal is much more plentiful than hard coal (anthracite). Lignite and peat may become increasingly important as the supply of higher grades of coal is depleted.

The supply of coal is limited. The deposits that exist today are less than 600 million years old. For a part of that time, the Earth was much warmer than it is now, and plant life flourished. Most plants lived, died, and decayed—playing their normal role in the carbon cycle (**figure 10.1**). But a small portion of the plant material became buried under mud and water. There, in the absence of oxygen, it could decay only partially. The structural material of plants is largely cellulose (chapter 16), a compound of carbon, hydrogen, and oxygen. Under the action of increasing pressure, as the material was buried more deeply, the cellulose molecules broke down. Small molecules rich in hydrogen and oxygen escaped, leaving behind a material increasingly rich in carbon. Thus, peat is a young coal, only partly converted. Anthracite, on the other hand, has been nearly completely carbonized.

Table 10.1
Typical (approximate) composition in percentages by weight of various grades of coal
(dry basis)

Grades of Coal	Carbon	Hydrogen	Oxygen	Nitrogen
Wood (included as a comparison)	50	6	43	1
Peat	59	6	33	2
Lignite (brown coal)	69	5	25	1
Bituminous (soft coal)	80 to 89	5	5 to 15	1
Anthracite (hard coal)	95	2 to 3	2 to 3	Trace

Data from "Zabetakis, M. G., and Phillips, L. D., *Coal Mining*. Washington, D.C.: United States Government Printing Office, 1975.

Presumably, fossil fuels are still being formed in nature. This process is perhaps most evident in peat bogs. The rate of formation is extremely slow, however. In fact, it has been estimated that we are using fossil fuels 50 000 times as fast as they are being formed.

People probably have used small amounts of coal since prehistoric times, but, as late as 1760, wood was for practical purposes the only fuel being used. In only a few hundred more years, we will have removed from the Earth and burned virtually all the remaining recoverable fossil fuels. Of all that ever existed, we will use about 90%

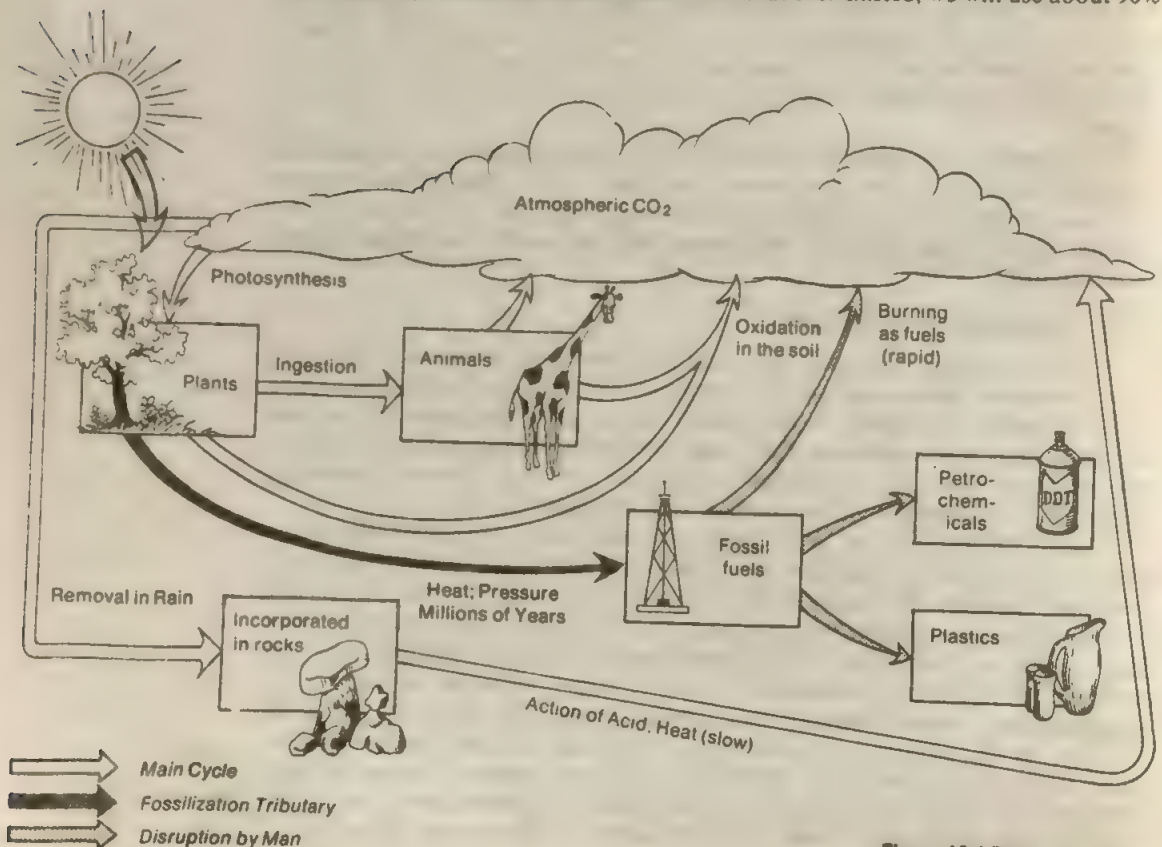


Figure 10.1 The carbon cycle.



Figure 10.2 Giant ferns, reeds, and grasses that grew during the Pennsylvanian period 300 million years ago helped form the coal we burn today. (Courtesy of the National Coal Association.)

in a period of 300 years. On a geological time scale, that is but a moment. Even on a historical basis, the fossil fuel feast is but a brief interlude.

We discuss coal as a source of energy in chapter 12. Coal is also a source of chemicals. When coal is heated in the absence of air, volatile material is driven off and a much purer form of carbon is left behind, although the carbon still is mixed with a small amount of mineral matter. This purified carbon is called *coke*. Vast quantities of coke are used in industry, chiefly to obtain metals from their ores.

Part of the volatile material given off in the coking process is condensed into *coal tar*. This gooeey mixture is an important source of organic chemicals, particularly aromatic compounds. We discuss some of these chemicals later in this chapter. For now, though, let's look at some of the simple compounds of carbon and hydrogen.

Millions of Hydrocarbons: The Unique Carbon Atom

A unique property of the carbon atom is its ability to bond to another carbon atom and that atom in turn to another carbon atom and so on. In this way, carbon atoms hook up to form long chains of hundreds or even thousands of atoms. This process is called *catenation*. No other element can form chains longer than four or five atoms. The chains can form branches and even rings of carbon atoms. This property makes possible a nearly endless number of hydrocarbons (compounds that contain only carbon and hydrogen).

Carbon, near the middle of the periodic chart, also bonds strongly to other elements, such as oxygen and nitrogen. Thus, carbon forms a vast array of compounds with chains of various lengths and rings of various sizes, each with a variety of other constituent and substituent atoms. Some of these, as we see in later chapters, are vital to life processes. Indeed, life itself is a property of some of these compounds.



Figure 10.3 This fossil is part of a fern frond (or leaf) of the genus *Pecopteris*, a very common plant in the coal swamps of 300 million years ago. It was found in the shale just above a coal seam in Wilmington Township, Will County, Illinois. (Courtesy of the National Coal Association.)

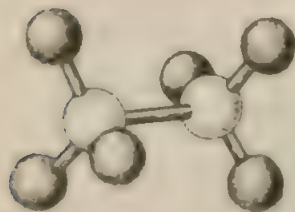
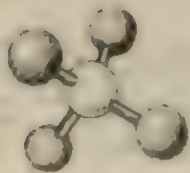
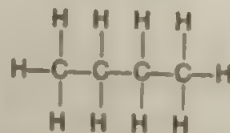
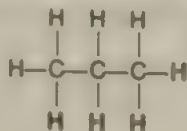


Figure 10.4 Ball-and-stick models of methane and ethane.

Alkanes: The Saturated Hydrocarbons

The nearly infinite variety of hydrocarbons is merely hinted at here. Before you can even begin to understand the large, complex molecules on which life is based, it is necessary to learn something about simpler molecules. In chapter 5, we encountered compounds called methane (CH_4) and ethane (C_2H_6). Models of molecules of these two compounds are shown in figure 10.4. These are the first two members of a series of related compounds called *alkanes* or *saturated hydrocarbons*. These are compounds in which there are only single bonds. (The meaning of this statement should be clearer after we have considered other classes of hydrocarbons.)

The next members of the alkane series are propane (C_3H_8) and butane (C_4H_{10}). Their structures are generally written



Actually, there are *two* butanes. The one above is called *normal* butane (or *n*-butane). The other, in which the carbon chain is *branched*, is called isobutane.

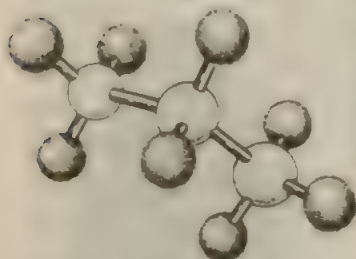
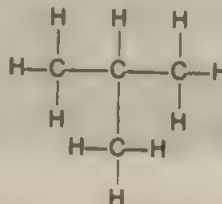


Figure 10.5 Ball-and-stick model of propane.

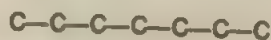
Note that both *n*-butane and isobutane have the same formula (C_4H_{10}) but they have different *structures*. Substances related in this way are called *isomers*. Isomers are very common in the compounds of carbon.

Propane and the butanes are familiar fuels. They usually are supplied under pressure in tanks. Although they are gases at ordinary temperatures and under normal atmospheric pressure, they are liquefied under pressure and are sold as liquefied petroleum gas (LP gas).

There are a great many other alkanes. The names, the molecular formulas, and the structural formulas for the *normal* isomers of several alkanes are given in table 10.2.

As incredibly complex as hydrocarbon chemistry may appear to you, there is some system to it. For example, from pentane on up, the first part of the name indicates the number of carbon atoms in the molecules. These names are based on prefixes derived from the Greek names for the numbers (summarized in table 10.3).

The ending of the name also has meaning. Note that all end in *-ane*. This indicates that all are *alkanes*. The name *heptane*, then, means an alkane with seven carbon atoms. To draw the structure of *n*-heptane, you merely write out a string of seven carbon atoms.



Then you attach enough hydrogens to the carbons to give each carbon a valence of 4. This requires three hydrogens on each end carbon and two each on the others.

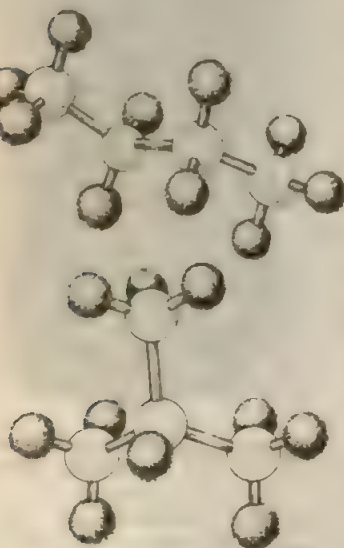


Figure 10.6 Ball-and-stick models of *n*-butane and isobutane.

Table 10.2
The first 10 normal alkanes

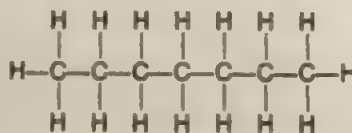
<i>Name</i>	<i>Molecular Formula</i>	<i>Structural Formula</i>	<i>Number of Possible Isomers</i>
Methane	CH ₄	<pre> H H — C — H H </pre>	1
Ethane	C ₂ H ₆	<pre> H H H — C — C — H H H </pre>	1
Propane	C ₃ H ₈	<pre> H H H H — C — C — C — H H H H </pre>	1
Butane	C ₄ H ₁₀	<pre> H H H H H — C — C — C — C — H H H H H </pre>	2
Pentane	C ₅ H ₁₂	<pre> H H H H H H — C — C — C — C — C — H H H H H H </pre>	3
Hexane	C ₆ H ₁₄	<pre> H H H H H H H — C — C — C — C — C — C — H H H H H H H </pre>	5
Heptane	C ₇ H ₁₆	<pre> H H H H H H H H — C — C — C — C — C — C — C — H H H H H H H H </pre>	9
Octane	C ₈ H ₁₈	<pre> H H H H H H H H H — C — C — C — C — C — C — C — C — H H H H H H H H H </pre>	18
Nonane	C ₉ H ₂₀	<pre> H H H H H H H H H H — C — C — C — C — C — C — C — C — C — H H H H H H H H H H </pre>	35

Table 10.2 (continued)

Name	Molecular Formula	Structural Formula	Number of Possible Isomers
Decane	$C_{10}H_{22}$	<pre> H H H H H H H H H H H - C - C - C - C - C - C - C - C - C - C - H H H H H H H H H H H </pre>	75

Table 10.3
Greek prefixes

Prefix	Number
Pent-	5
Hex-	6
Hept-	7
Oct-	8
Non-	9
Dec-	10



Notice that in **table 10.2** each molecular formula differs from the one preceding it by precisely one carbon atom and two hydrogens; that is by a CH_2 group. Such a series of compounds has properties that vary in a regular and predictable manner. This principle, called *homology*, gives meaning to *organic chemistry* in much the same way that the periodic table gives organization and meaning to the chemistry of the elements. Instead of studying the chemistry of a bewildering array of individual carbon compounds, organic chemists study a few members of a homologous series from which they can *deduce* the properties of other compounds in the series.

One other point before leaving **table 10.2**: not all the possible isomers of the larger molecules have been isolated. Indeed, the task rapidly becomes even more prohibitive as you proceed up the series. There are, for example, over 4 billion possible isomers with the molecular formula $C_{30}H_{62}$.

On Rings and Things

The hydrocarbons we have encountered so far (alkanes) have been composed of open-ended chains of carbon atoms. Carbon and hydrogen atoms also can hook up in other arrangements, some of them quite interesting. There is a synthetic hydrocarbon that has the formula C_3H_6 . The three carbons are joined in a ring, or a cycle. The synthetic hydrocarbon is called *cyclopropane*. In addition to its interesting structure, cyclopropane has some intriguing properties. For one, it can be used as an anesthetic, since, when it is inhaled, it renders humans unconscious and unaware of pain. Also it is explosive when mixed with air (so care must be taken to avoid having flames or sparks in an operating room where it is being used).

There are many such cyclic compounds. We encounter more of them as we proceed. In fact, the DNAs of some viruses are known to be cyclic molecules, molecules in which hundreds of thousands of carbon, nitrogen, oxygen, hydrogen, and phosphorus atoms are joined in twisted strands like necklaces made of tiny beads.

Unsaturated Hydrocarbons: Alkenes and Alkynes

Two carbon atoms can share more than one pair of electrons. In ethylene (C_2H_4), the two carbon atoms share *two* pairs of electrons and the carbon atoms are joined by a *double bond*.

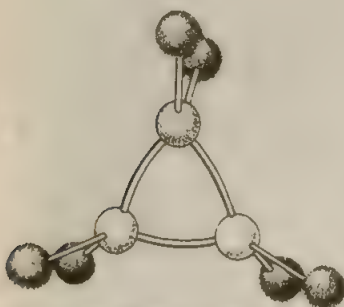
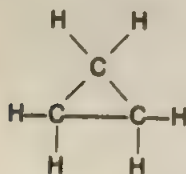


Figure 10.7 Ball-and-stick model of cyclopropane.

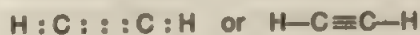


Cyclopropane



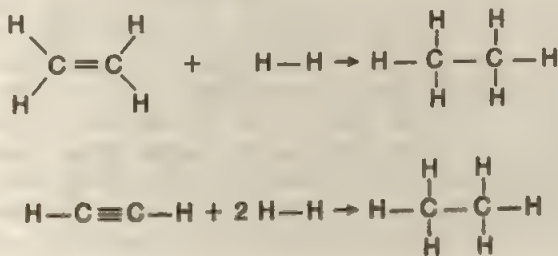
Ethylene is one of the most important of all commercial chemicals. In 1978, the United States chemical industry produced 13 billion kg of ethylene, making it the most important of all synthetic organic chemicals. Over 33% went into the manufacture of polyethylene, one of the most familiar plastics. Another 17% or so was converted to ethylene glycol, the major component of most brands of anti-freeze for automobile radiators.

In acetylene (C_2H_2), the two carbon atoms share *three* pairs of electrons; the carbon atoms are joined by a *triple bond*.



About 10% of the acetylene produced in the United States is used in oxy-acetylene torches for cutting and welding metals. Such torches can produce very high temperatures. Most acetylene, however, is converted to chemical intermediates that are, in turn, used to make vinyl and acrylic plastics, fibers, and resins and a variety of other chemical products. Acetylene is even a part of the molecular architecture of birth-control pills (chapter 22).

Ethylene is the first member of a family of hydrocarbons called *alkenes*. Each alkene contains a carbon to carbon double bond. Similarly, acetylene is the first member of the *alkyne* family. Each alkyne contains a triple bond. Collectively, alkenes and alkynes are called *unsaturated hydrocarbons* because they can add more hydrogen atoms to form saturated hydrocarbons (alkanes).



We discuss unsaturated fats in chapter 16. These compounds, like the alkenes, contain carbon to carbon double bonds.

Of Benzene . . . and Dozing by the Fire

Still another type of hydrocarbon is represented by the compound benzene. Benzene was first isolated from a whale oil by-product by Michael Faraday in 1825. (This is the same Michael Faraday whose electrolysis experiments are described in chapter 3.) Benzene's molecular formula soon (1834) was determined to be C_6H_6 . We can write many structures corresponding to the formula C_6H_6 . Three possible structures are shown. All of these follow the valence rule; that is, each carbon atom has four bonds and each hydrogen has one bond. These structures (and others that were proposed) indicate that benzene, like ethylene and acetylene, is *unsaturated*. But benzene doesn't act unsaturated; it doesn't add hydrogen readily.

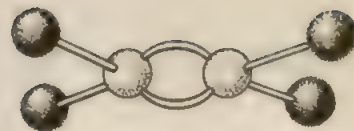
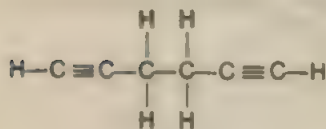
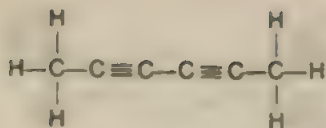


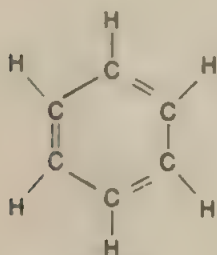
Figure 10.8 Ball-and-stick model of ethylene.



Figure 10.9 Ball-and-stick model of acetylene.

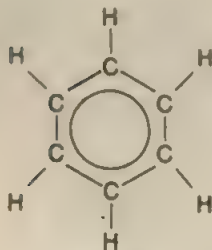


Three possible representations of benzene



Benzene

(Kekulé's representation)



Benzene

(modern representation)

It wasn't until 1865 that Friedrich August Kekulé, a German chemist, proposed a satisfactory structure for benzene. One day, while dozing by the fire, he saw chains of atoms whirling in a dance. Suddenly, one of the snakes of atoms seized its own tail and formed a swirling ring. Until Kekulé's vision, chemists had thought only of chains of carbon atoms. Afterward, they came to envision rings of atoms as well. (Cyclopropane, mentioned earlier, was not prepared until 1881.) Kekulé proposed a structure with alternate double and single bonds. (Kekulé's dream didn't come out of the blue; he had been puzzling over the problem for weeks.)

Friedrich August Kekulé was an architecture student who later turned to chemistry. He became professor of chemistry at Ghent in Belgium and at Heidelberg and Bonn in Germany. According to Kekulé's own account of his dream (reference 2):

"During my stay in Ghent I resided in elegant bachelor quarters. My study, however, faced a narrow side-alley and no daylight penetrated it. For the chemist who spends his day in the laboratory this mattered little. I was sitting writing at my textbook but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire and dozed. Again the atoms were gamboling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of the kind, could now distinguish larger structures of manifold conformation: long rows, sometimes more closely fitted together, all twining and twisting in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke; and this time also I spent the rest of the night in working out the consequences of the hypothesis.

"Let us learn to dream, gentlemen, then perhaps we shall find the truth. But let us beware of publishing our dreams till they have been tested by the waking understanding."

As great an achievement as coming up with this structure for benzene was, the structure is no longer regarded as satisfactory. Modern chemists, using quantum theory, realize that the extra or double bond electrons couldn't be located between specific carbon atoms but must be shared equally by all six carbon atoms. The modern representation of benzene uses a circle to represent the extra electrons.

Benzene is a liquid at room temperature. It is used widely as a solvent and as an intermediate product in the production of other aromatic compounds. United States production in 1978 was 5.06 billion kg. Benzene is thought to cause leukemia in workers exposed to it over the years, and its use may be severely restricted in the future.

On the Laziness of Chemists and Typists: More Symbolism

It takes time to draw out structures such as those we have used for butane, cyclopropane, ethylene, and benzene. They are also difficult to type. Therefore, chemists usually resort to condensed structures, such as $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ for butane and $\text{CH}_2=\text{CH}_2$ for ethylene; and sometimes they even resort to a rather mystical sort of symbolism. For example: a chemist notes that the three carbon atoms of cyclopropane form a triangle; therefore, he or she uses a triangle to represent cyclopropane. Similarly, the six carbons of benzene form a hexagon; therefore, a hexagon (with extra lines to represent double bonds or, in the modern picture, a circle to represent the six unassigned electrons) represents benzene (figure 10.10).

Remember that the real benzene (a gasolinelike liquid) is not really like the structure in figure 10.10. No one has ever seen a benzene molecule. The structure represents a concept of a benzene molecule.



Figure 10.10 Chemical symbolism.

There are many compounds chemically similar to benzene. Several of those discovered in the early days had pleasant odors. These were called *aromatic* compounds. The label *aromatic* used today simply means a compound related to benzene and does not imply a pleasing aroma. In fact, some are odorless and others stink.

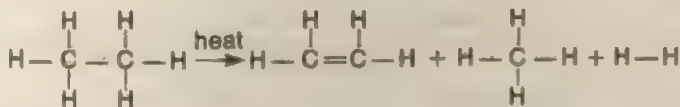
Natural Gas: Mostly Methane but Much More

Natural gas is a fossil fuel. It is composed principally of methane, but its composition varies greatly. In North America, natural gas typically contains 60% to 80% methane, 5% to 9% ethane, 3% to 18% propane, and 2% to 14% butane and pentane. In Europe, methane is essentially the only hydrocarbon in natural gas. The gas, as it comes from the ground, often contains sulfur compounds and nitrogen as impurities.

Natural gas was most likely formed, ages ago, by the action of heat, pressure, and perhaps bacteria on buried organic matter. The gas is trapped in geological formations capped by impermeable rock. It is removed through wells drilled into the gas-bearing formations.

Most natural gas is used as fuel, but it is also an important raw material. In North America, part of the higher alkanes is separated out of the natural gas. Ethane and propane are *cracked*—decomposed by heat in the absence of air—to form ethylene and propylene. These alkenes are intermediates in the synthesis of plastics (chapter 14) and many other useful commodities.

Cracking breaks chemical bonds and allows new ones to form. Cracking of ethane produces hydrogen and some methane in addition to ethylene. (The equation is not balanced; the proportion of products varies with conditions.)



A small amount of higher alkanes also is formed by the combination of fragments formed in cracking.

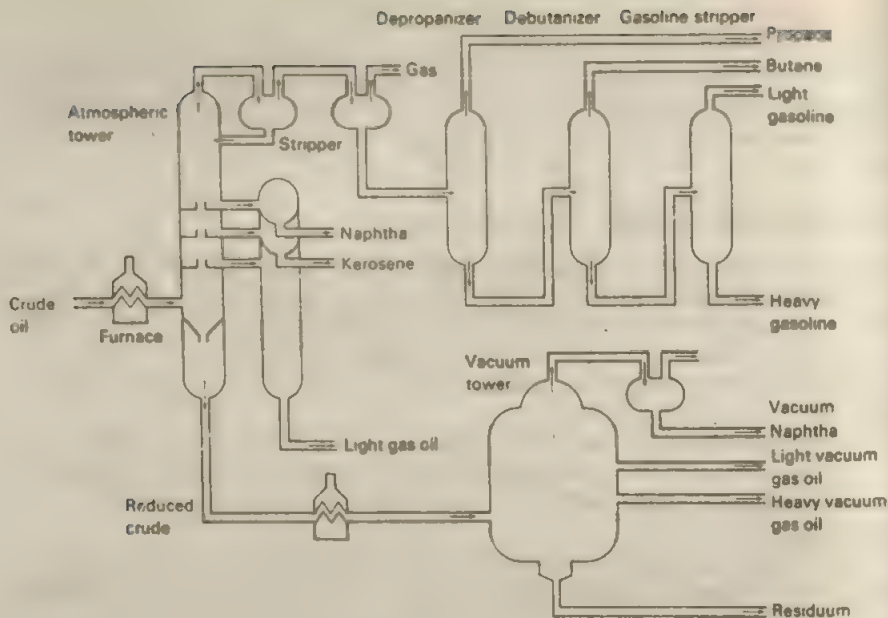
Other products from natural gas include acetylene, hydrogen cyanide ($\text{H}-\text{C}\equiv\text{N}$), chlorinated hydrocarbons, methyl alcohol, and ammonia. These in turn, have a variety of uses. Acetylene we have already considered. The others are discussed in following chapters.

Petroleum: Liquid Hydrocarbons

Petroleum is an exceedingly complicated liquid mixture of organic compounds. The main components are hydrocarbons. These are chiefly alkanes, but some are cyclic compounds. Petroleum also has varying proportions of sulfur-, nitrogen-, and oxygen-containing compounds.

We have seen that coal is primarily of plant origin. Recent evidence indicates that petroleum is of animal origin. Most likely it is formed primarily from the fats (chapter 16) of ocean-dwelling, microscopic animals, for it is nearly always found in rocks of oceanic origin. Fats are made up mainly of compounds of carbon and hydrogen, with a little oxygen (e.g., $\text{C}_{57}\text{H}_{110}\text{O}_6$). The removal of the oxygen and the slight rearrangement of the carbon and hydrogen atoms in these fats produces typical hydrocarbon molecules as they occur in petroleum. Petroleum, as it comes from the ground, is of limited use. To make it better suit our needs, we separate it into fractions by boiling it in a distillation column (figure 10.11). The lighter molecules, those with 1 to 4 carbon atoms each, come off at the top of the column.

Figure 10.11 The fractional distillation of petroleum.



The next fraction contains, for the most part, molecules with 5 to 12 carbon atoms. These and the other fractions are listed in table 10.4.

Table 10.4
Typical petroleum fractions

Fraction	Typical Range of Hydrocarbons	Approximate Range of Boiling Point (in degrees Celsius)	Typical Uses
Natural gas	CH_4 to C_4H_{10}	Less than 40	Fuel, starting materials for plastics
Gasoline	C_5H_{12} to $\text{C}_{12}\text{H}_{26}$	40–200	Fuel, solvents
Kerosene	$\text{C}_{12}\text{H}_{26}$ to $\text{C}_{16}\text{H}_{34}$	175–275	Diesel fuel, jet fuel, home heating; cracking to gasoline
Heating oil	$\text{C}_{15}\text{H}_{32}$ to $\text{C}_{18}\text{H}_{38}$	250–400	Industrial heating, cracking to gasoline
Lubricating oil	$\text{C}_{17}\text{H}_{36}$ and up	Above 300	Lubricants
Residue	$\text{C}_{20}\text{H}_{42}$ and up	Above 350 (some decomposition)	Paraffin, asphalt

Since gasoline is the fraction most in demand, the fractions that boil at higher temperatures are often in excess supply. These are often converted to gasoline by heating in the absence of air. This cracking process breaks down the bigger molecules into smaller ones. The effects of the process, with $\text{C}_{14}\text{H}_{30}$ as an example, are illustrated in figure 10.12.

Not only does cracking convert part of the molecules into those in the gasoline range (C_5H_{12} through $\text{C}_{12}\text{H}_{26}$), it produces a variety of useful by-products. The

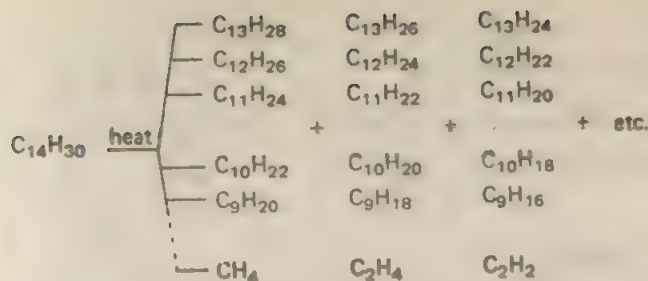


Figure 10.12 Formulas of some of the products formed when $\text{C}_{14}\text{H}_{30}$ (a typical molecule in kerosene) is cracked. You need only note that a great variety of hydrocarbons with fewer carbon atoms are formed.

Smaller
saturated
hydrocarbons
(having from
1 to 13 carbon
atoms)

Unsaturated
hydrocarbons
(having from
2 to 13 carbon
atoms)

unsaturated hydrocarbons are starting materials for the manufacture of many plastics, detergents, and drugs—indeed, a whole host of petrochemicals.

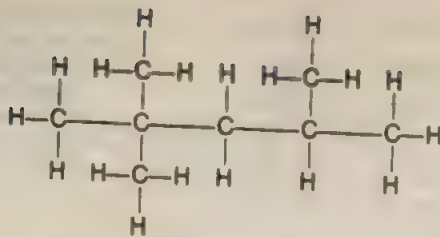
The cracking process described here is a crude, yet illustrative example of how chemists modify nature's materials to meet human needs and desires. Starting with coal tar or petroleum, a chemist can create a dazzling array of substances with a wide variety of properties. A few of these substances are plastics, pesticides, herbicides, perfumes, preservatives, pain killers, antibiotics, stimulants, depressants, and detergents. Many of these substances are discussed in other chapters. A chemist's ability to create new substances from petroleum products enables us to select materials that more closely suit our specifications. Chemists provide the options; all of us make the choices. The use of petroleum as a source of energy is discussed in chapter 12.

Gasoline: From the Refinery to the Chemist

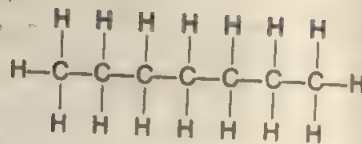
Gasoline, like the petroleum from which it is derived, is a mixture of hydrocarbons. The typical alkanes in gasoline have formulas ranging from C_5H_{12} to $\text{C}_{12}\text{H}_{26}$. Since there are many isomeric forms, particularly for the higher members of the group, we see that gasoline is an exceedingly complex mixture of alkanes. There are also small amounts of other kinds of hydrocarbons and even some sulfur- and nitrogen-containing compounds present. The gasoline fraction of petroleum as it comes from the refinery is called *straight-run gasoline*. It doesn't burn very well in modern, high-compression automobile engines. Chemists have learned how to modify it in a variety of ways to make it burn better.

Upping the Octane Rating

Early in the development of the automobile engine, scientists learned that some types of hydrocarbons burned more evenly and were less likely to ignite prematurely than others. Ignition before the piston was in proper position led to a knocking in the engine. Scientists soon were able to correlate good performance with a branched-chain structure in hydrocarbon molecules. An arbitrary performance standard was established in 1927. The best performer in a laboratory test engine was found to be a compound that became known as *isooctane* because it was one of 18 isomeric octanes. Isooctane was assigned a value of 100 octane. An unbranched-chain compound, *n*-heptane, was found to cause a very bad knock. It was given a rating of 0. A gasoline rated 90 octane was one that performed the same as a mixture that was 90% isooctane and 10% *n*-heptane.

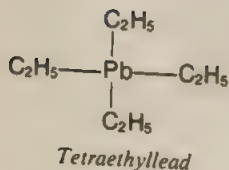
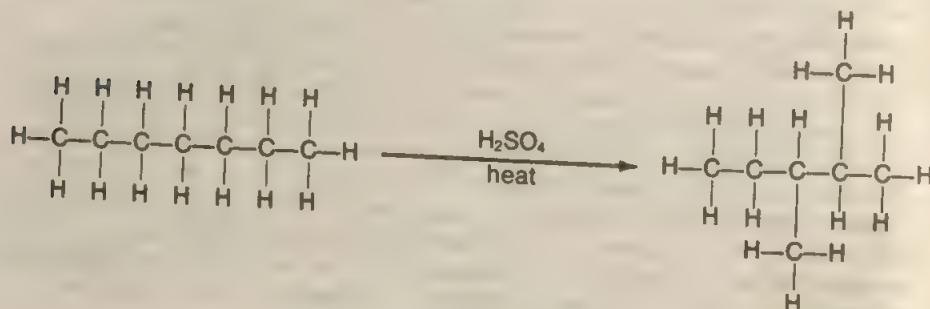


Isooctane



n-Heptane

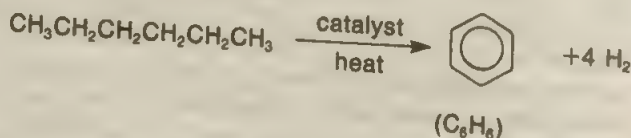
During the 1930s, chemists discovered that the octane rating of gasoline could be improved by heating gasoline in the presence of certain catalysts (see chapter 8), such as sulfuric acid (H_2SO_4) and aluminum chloride (AlCl_3). This increase in octane rating was attributed to a conversion (*isomerization*) of a part of the unbranched structures to highly branched molecules. For example *n*-heptane molecules could be isomerized to a branched structure.



Chemists also are able to combine small hydrocarbon molecules (below the gasoline range) into larger ones more suitable for use as fuel.

Certain chemical substances also were discovered that, when added in small amounts, substantially improved the antiknock quality of gasoline. Chief among these *additives* was tetraethyllead. This compound, when added in amounts as small as 1 mL per litre of gasoline (about 0.1 fl oz per gallon, or 1 part per thousand), would increase the octane rating from approximately 55 to 90 or more.

However, lead is toxic. Large amounts of it enter the environment through the combustion of leaded gasoline in automobiles. Further, lead fouls the catalytic converters used in modern automobiles. To get high octane ratings in unleaded fuels, petroleum refineries use *catalytic reforming* to convert low-octane alkanes to high-octane aromatic compounds. For example, hexane with an (octane number of 25) is converted to benzene (with an octane number of 106).



Air-pollution problems associated with automobiles are discussed in chapter 19.

To recapitulate briefly, American scientists were able, by World War II, to convert nearly all petroleum fractions into gasoline. Furthermore, they were able to improve octane ratings substantially by rearranging the molecules and adding tetraethyllead. It was this high-performance fuel, as much as or more so than

superior machines, that made possible the Allied victory in the air war with the Axis powers during World War II.

The petroleum industry's ability to modify hydrocarbon molecules enables them to produce increased amounts of whatever fraction they desire. They can, on demand, produce more fuel oil or more gasoline. They can even make gasoline from coal (chapter 13). They can't, however, increase the amount of fossil fuels aboard Spaceship Earth. And we are using these irreplaceable natural resources at a rapid and ever-increasing rate. Let's hope that scientists soon develop new sources of energy that do not depend on petroleum, so that we can stop what is in many ways a profligate waste of irreplaceable natural resources. Spaceship Earth has aboard it all the supplies it will ever have. We must use them wisely.

Problems

1. What is the principal difference in chemical composition between anthracite and bituminous coal?
2. How have people modified the carbon cycle?
3. List two characteristics of the carbon atom that make possible the existence of millions of carbon compounds.
4. Write the structures for the following hydrocarbons.
 - a. *n*-pentane
 - b. propane
 - c. *n*-butane
 - d. isobutane
5. Write the structure for cyclopentane (C_5H_{10}).
6. In June of each year, *Chemical and Engineering News* publishes a list of the top 50 industrial chemicals. Look in the most recent June issue and find the annual production of each of the following chemicals.
 - a. acetylene
 - b. ethylene
 - c. benzene
 - d. ammonia
 - e. methanol
 - f. cyclohexane
7. Propylene, like ethylene, is an alkene. Its molecular formula is C_3H_6 . Write a structure for propylene. Be sure to follow the valence rules (carbon forms four bonds, hydrogen only one).
8. Define and give an example of each of the following terms.
 - a. hydrocarbon
 - b. alkane
 - c. saturated hydrocarbon
 - d. unsaturated hydrocarbon
 - e. aromatic hydrocarbon
 - f. isomers
 - g. fossil fuel
 - h. cracking
9. How is crude petroleum modified to better meet our needs and wants?
10. What are some possible sources of petrochemicals—for manufacturing drugs, plastics, detergents, and such—when our petroleum reserves are gone?
11. The complete combustion of benzene forms carbon dioxide and water.



Balance the equation. What weight of carbon dioxide is formed by the complete combustion of 39 g of benzene?

12. What weight of carbon dioxide is formed by the combustion of 1250 kg of coal when the coal is 40% carbon? The equation is



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chapter 11

Organic Chemistry: Some Hors d'Oeuvres

In the last chapter, we discussed the chemistry of coal, natural gas, and petroleum—all materials derived from organisms that lived in ages past. In this chapter and some of those that follow, we consider the chemistry of present-day organisms and we take a look at the chemistry of life.

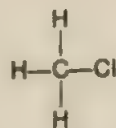
As you might guess, the chemistry of life is extremely complex. Rather than jump right into the middle of that complexity, we introduce several simple families of organic compounds. In each, we start with some simple compounds and then move on to some that are more complicated and perhaps more interesting. Don't assume that you will be bored by the small molecules, though. Some of them have fascinating properties of their own.

The Chlorinated Hydrocarbons: Many Uses, Some Hazards

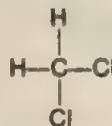
Now that you know what hydrocarbons are, let's look at some chlorinated hydrocarbons. When chlorine gas (Cl_2) is mixed with methane (CH_4) in the presence of ultraviolet light, a reaction takes place at a very rapid (even explosive!) rate. The result is a mixture of products, some of which are probably quite familiar to you.

Methyl chloride is used as a refrigerant and a chemical intermediate. Methylene chloride is an important solvent. It is used, for example, to extract caffeine from coffee to make the decaffeinated brands.

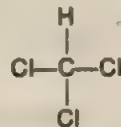
Chloroform was used as an anesthetic in earlier times, but such use is now considered quite dangerous. The dosage required for effective anesthesia is too close to a lethal dose. Carbon tetrachloride has been used as a dry-cleaning solvent and in fire extinguishers. It is no longer recommended for either use. Exposure to carbon tetrachloride (or most of the other chlorinated hydrocarbons, for that matter) can cause severe damage to the liver. Even the vapor, breathed in small amounts, can cause serious illness when the exposure is prolonged. Use of a carbon tetrachloride fire extinguisher in conjunction with water to put out a fire can be deadly. Carbon tetrachloride reacts with water to form phosgene (COCl_2), an extremely poisonous gas. In fact, phosgene was used in poison gas warfare during World War I. Recent evidence also indicates that both carbon tetrachloride and chloroform can cause cancer when they are ingested.



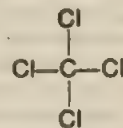
*Methyl
chloride*



*Methylene
chloride*



Chloroform

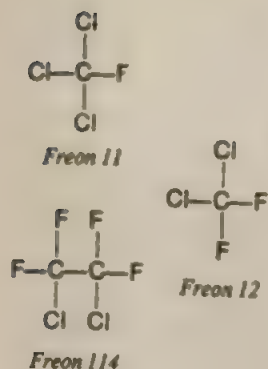


*Carbon
tetrachloride*

A variety of more complicated chlorinated hydrocarbons are of considerable interest. DDT (dichlorodiphenyltrichloroethane) and other chlorinated hydrocarbons used as insecticides are discussed in chapter 15. In chapter 14, we study the PCBs (polychlorinated biphenyls). For now, let's just say that all chlorinated hydrocarbons have similar properties. Most are only slightly polar, and they do not dissolve in water, which is highly polar. Instead, they dissolve (and *dissolve* in since solubilities are reciprocal) fats, oils, greases, and other substances of low polarity. That is why certain chlorinated hydrocarbons make good dry-cleaning solvents; they remove grease and oily stains from fabrics. That is also why DDT and PCBs cause problems for fish and birds and perhaps for people; the toxic substances are concentrated in fatty animal tissues.

The Chlorofluorocarbons: Spray Cans and Skin Cancer

Compounds containing fluorine as well as chlorine have been used as the dispersing gases in aerosol cans and as refrigerants. Properly called *chlorofluorocarbons*, they are perhaps best known as *Freons*, from their du Pont trade name. Structures of three of the Freons are illustrated here. At room temperature, the chlorofluorocarbons are gases or liquids with low boiling temperatures. They are essentially insoluble in water and inert toward most other substances. These properties make them ideal propellants for use in aerosol cans of deodorants, hair sprays, and food products. Unfortunately, the inertness of these compounds allows them to persist in the environment. They diffuse into the stratosphere, where they undergo chemical reactions that may lead to the destruction of the ozone layer, which protects the Earth from harmful ultraviolet radiation. A decrease in the amount of ozone in the stratosphere might lead to an increase in the incidence of skin cancer. We look at this problem in more detail in chapter 19.



The Alcohols: From Booze to Beeswax

We have seen that one or more hydrogen atoms of a hydrocarbon can be replaced by chlorine. Since both hydrogen and chlorine are univalent, this is a reasonable substitution. Other atoms, or even groups of atoms, also may substitute for hydrogen. Let's look at one such group of atoms, the *hydroxyl* ($-\text{OH}$) group.

First, let's play the molecular architect game again. Wood alcohol (CH_4O) is made by heating wood (in the absence of air) until it breaks down and then collecting the vapors formed. This process is called *destructive distillation*. A number of other chemical substances are formed as well as wood alcohol. What is the structure of wood alcohol? The parts list is:

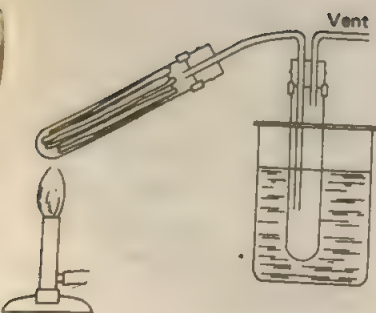
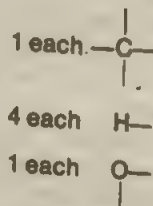
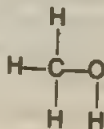


Figure 11.1 An apparatus for the destructive distillation of wood. The wood is heated in an enclosed tube, and alcohol is condensed in the second tube by the cold water in the beaker. Gases formed in the process can be burned as they emerge through the vent tube.



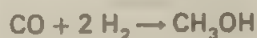
There is only one way in which these can be put together.



This compound also is called methyl alcohol or simply methanol. Notice that it is related to methane in that one hydrogen of methane has been replaced by that —OH group.

Methyl alcohol is extremely toxic.* Even as little as a 1-oz. (30-mL) shot can cause permanent blindness or death. Many accidents each year are attributed to mistaking this alcohol for its less harmful relative, ethyl alcohol, the intoxicating ingredient of beverages such as beer, wine, whiskey, vodka, and brandy.

Methanol is made commercially mainly by reacting carbon monoxide with hydrogen.



The reaction is carried out at a high temperature and pressure and in the presence of a catalyst. Despite its toxicity, methanol is a valuable industrial solvent. It is also a raw material for the production of other chemicals.

*The common term *poison* is applied to a variety of substances, often without any indication of *degree* of toxicity. To avoid this uncertainty, biochemists use the term LD_{50} to indicate the dosage that would be lethal to 50% of a population of test animals. This dosage is expressed in terms of amount of drug per kilogram of body weight. The LD_{50} for humans usually can only be estimated.

Extrapolation from toxicity in rats or rabbits to toxicity in people can only be approximate at best. What is toxic in rats may not be as toxic in humans. Or it might be more toxic. However, general trends in toxicity usually can be judged from animal studies. Toxicities of some alcohols are listed in table 11.1.

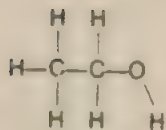
Table 11.1
Lethal doses (orally) of some alcohols in rats

Alcohol	Structure	LD_{50} (in grams per kilogram of body weight)
Methanol	CH_3OH	—
Ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	13.7
1-Propanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	1.87
2-Propanol	$\text{CH}_3\text{CHOHCH}_3$	5.8
1-Butanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	4.36
1-Hexanol	$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{OH}$	4.9
Ethylene glycol	$\text{HOCH}_2\text{CH}_2\text{OH}$	8.54
Glycerol	$\text{HOCH}_2\text{CHOHCH}_2\text{OH}$	31.5

Note 1. These data are taken from *The Merck Index*. See Reference 11.

Note 2. No LD_{50} is given for methanol. Its acute (short term) toxicity is not terribly high. However, it is metabolized to formaldehyde (HCHO) in the body. The chronic (long term) toxicity is quite high due to this metabolite. The LD_{50} for formaldehyde administered orally to rats is 0.070 gram per kilogram of body weight. The LD_{50} for acetaldehyde, the metabolite of ethanol, is only 1.9 g/kg.

Ethyl alcohol is toxic, too. One pint of pure ethyl alcohol, rapidly ingested, would kill most people. Even the strongest alcoholic beverages, however, are seldom

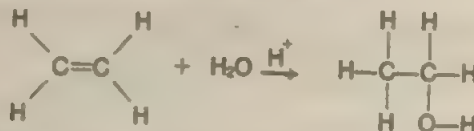


Ethyl alcohol

more than 45% ethyl alcohol, or 90 proof.* Excessive ingestion over a long period of time leads to deterioration of the liver and loss of memory, and it can lead to strong physiological addiction. Ethyl alcohol for beverages is made by the fermentation of grain or other starchy or sugary materials. Knowledge of this process goes far back into prehistory. Making ethyl alcohol is one of the oldest chemical procedures known.

Ethyl alcohol can be considered a derivative of ethane in which one H of the latter is replaced by an —OH group. Ethanol is another name for the compound.

In addition to its use as a beverage, ethyl alcohol is used in great quantities as an industrial solvent and as a starting material for other chemical products. Most industrial ethanol is prepared by the reaction of ethylene with water.



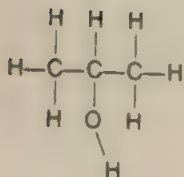
The H^+ over the arrow indicates that an acid (usually sulfuric) is used to catalyze the reaction. This is a striking example of how chemists can change materials to meet people's needs. Ethylene is a gas that has little use as it is. It is produced in great quantity as a by-product of the cracking of petroleum (chapter 10). By causing it to react with water, the chemist converts ethylene to a useful and valuable solvent. Ethylene is also a valuable starting material for the production of plastics (chapter 14).

Synthetic alcohol made from ethylene is not ordinarily used in beverages. In fact, to prevent its use in this manner, it is usually *denatured* by adding a poisonous or noxious substance. Among the common denaturants are gasoline and methanol.

Another alcohol familiar to most people is isopropyl alcohol, or rubbing alcohol. It is a derivative of propane, with the —OH replacing an —H on the central or number-2 carbon. Another name for the compound is 2-propanol. Rubbing alcohol is quite toxic, but ingestion is not especially dangerous because it induces severe vomiting. It doesn't stay down long enough to kill you, though it might stay down long enough to make you wish you were dead.

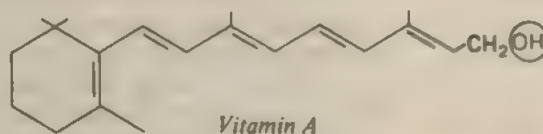
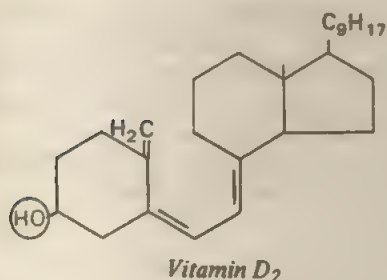
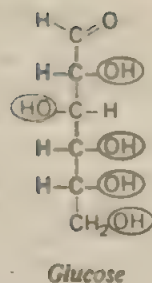
The alcohols, like the alkanes and other families of compounds, compose a homologous series that vary more or less regularly in their properties. All alcohols are characterized by the presence of a hydroxyl (—OH) group. This pair of atoms is called the *functional group* of the alcohols. Quite often, the formula ROH is used to indicate alcohols generally or collectively. The R stands for the hydrocarbon portion of the molecule. The —OH (the functional group) is the part of the molecule that is involved in the characteristic reactions of the alcohols. The functional group of an organic molecule is the site of most reactions that the molecule undergoes.

Many compounds of biological interest have the alcohol functional group. The sugars (chapter 16) and some of the chemicals in birth-control pills (chapter 22) are alcohols. Some other alcohols of interest are shown in **figure 11.2**. Don't let those



Isopropyl alcohol

*The *proof* is merely twice the percentage of alcohol by volume. The term has its origin in an old seventeenth-century English method for testing whiskey. Dealers were perhaps too often tempted to increase profits by adding water to the booze. A qualitative method for testing the whiskey was to pour some of it on gunpowder and ignite it. If the gunpowder ignited after the alcohol had burned away, that was considered "proof" that the whiskey did not contain too much water.



complicated structures scare you. All you need to be able to do is to see that each contains a hydroxyl group. The presence of a hydroxyl group makes each an alcohol.

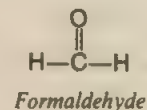
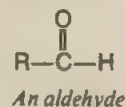
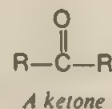
Next, we consider two related families of organic compounds, the aldehydes and the ketones. Both families are characterized by the presence of a carbon atom doubly bonded to an oxygen atom. This arrangement is called the *carbonyl functional group*. Aldehydes have a hydrogen atom attached to the carbonyl carbon; ketones have the carbonyl carbon attached to two other carbon atoms. If we let R stand for the hydrocarbon portions of molecules, we can write general formulas for aldehydes and ketones.

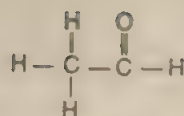
The simplest aldehyde is formaldehyde. It is a gas at room temperature, but it is readily soluble in water. As a 40% solution called *formalin*, it is used as a preservative for biological specimens. If you have ever been in a biology laboratory, you are no doubt familiar with the rather unpleasant odor of formaldehyde.

Formaldehyde is used to make certain plastics (chapter 14). It also is used to disinfect homes, ships, and warehouses. Commercially, formaldehyde is made by the oxidation of methanol. This is the same reaction that occurs in the human body when methanol is ingested (table 11.1).

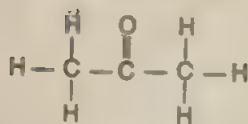
There are many aldehydes, but the only other that we need to mention here is acetaldehyde. This aldehyde is made by the oxidation of ethanol. This compound is probably responsible for the addictive nature of ethanol.

There are also many ketones, the simplest of which is called acetone. Acetone is a common solvent for such organic materials as fats, rubbers, plastics, and varnishes.

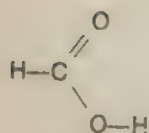




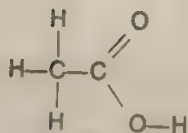
Acetaldehyde



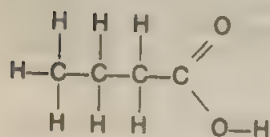
Acetone



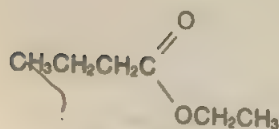
Formic acid



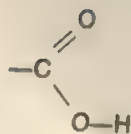
Acetic acid



Butyric acid



Ethyl butyrate



The carboxyl group

It also finds use in paint and varnish removers. It is the major (sometimes the only) ingredient of fingernail polish removers.

The Odorous World of Organic Acids

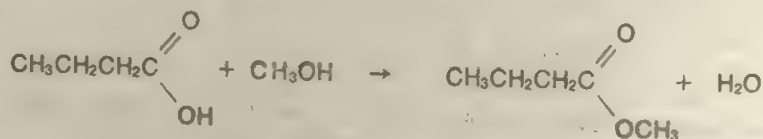
The familiar strong acids (chapter 7) such as sulfuric, hydrochloric, and nitric acids are called *mineral acids* because they are derived from inorganic materials. Many of the weak acids are organic ones. They were so named originally because they were derived from plant or animal sources, that is, from organisms. Nowadays, like other carbon compounds, they often are synthesized from coal tar or petroleum.

The simplest organic acid is formic acid. It was first obtained by the destructive distillation of ants (Latin *formica*; "ant"). The bite of an ant smarts because the ant injects formic acid as it bites. The stings of wasps and bees contain formic acid (as well as other poisonous materials).

Acetic acid can be made by the aerobic fermentation of a mixture of cider and honey. This produces a solution (vinegar) that contains about 4% to 10% acetic acid plus a number of other compounds that give vinegar its flavor. Acetic acid is probably the most familiar *weak acid* used in educational and industrial chemistry laboratories.

If you've ever smelled rancid butter, you probably wish you hadn't, but you know what butyric acid smells like. It is one of the most fantastically foul-smelling substances imaginable. Butyric acid can be isolated from butterfat or synthesized in the laboratory. It is one of the ingredients of body odor. Extremely small amounts of this and other chemicals enable bloodhounds to track fugitives.

Some derivatives, called *esters*, of this odorous chemical are used in flavors and perfumes. Methyl butyrate, made from butyric acid and methyl alcohol

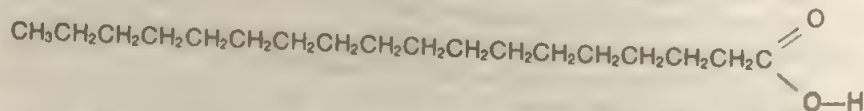


Butyric acid

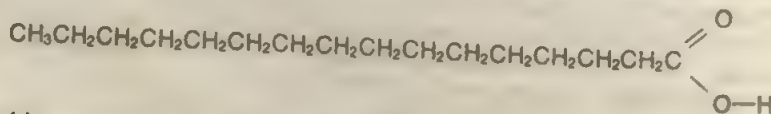
Methyl butyrate

is used in artificial rum and fruit flavors. Pineapple oil is a solution of ethyl butyrate in ethyl alcohol. What a difference a little change in the molecular architecture makes! From a foul, rancid odor to a pleasant fruity aroma by replacing an —OH group by a methoxy ($\text{CH}_3\text{O—}$) or an ethoxy ($\text{C}_2\text{H}_5\text{O—}$) group.

The functional group of the organic acids is called the *carboxyl group*. It is quite common in nature. Let's look at two more examples. Stearic acid ($C_{18}H_{35}O_2$) is a rather large molecule obtained from fat. Beef tallow is a particularly good source. The structure of stearic acid, in condensed form, is:

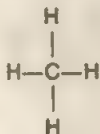


Palmitic acid ($C_{16}H_{32}O_2$) is obtained from palm oil. Its structure, condensed, is:

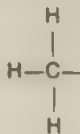


These big, complicated molecules are organic acids. Note the functional group on

The names of alkyl groups are derived from the parent alkane. The methyl group is considered to be derived from methane.

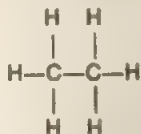


Methane

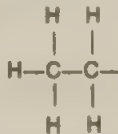


Methyl group

The ethyl group is derived from ethane in a like manner.

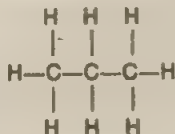


Ethane

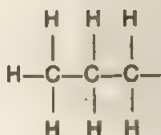


Ethyl group

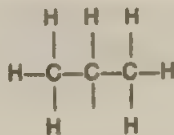
Two groups are derived from propane. One has its attachment through an end carbon, the other through the central carbon atom.



Propane



n-Propyl group



Isopropyl group

Names of alkoxy groups are similarly derived. $\text{CH}_3\text{O}-$ is derived from methane, and so it is a methoxy group. $\text{C}_2\text{H}_5\text{O}-$ is derived from ethane (C_2H_6), and so it is an ethoxy group.

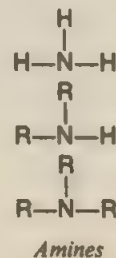
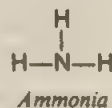
one end. The rest of the molecule is like a hydrocarbon. We will see these big fellows again, for they are the sort of fatty acids from which soap is derived.

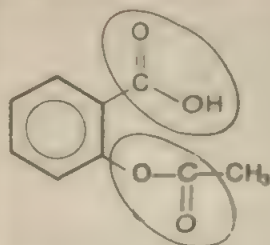
Some other acids and esters of interest are shown in figure 11.3. Again, be sure not to let the complicated structures scare you. You don't have to memorize them. Just look for the carboxyl group (abbreviated $-\text{COOH}$ in some of the structures) to identify an organic acid. In esters, the $-\text{OH}$ of the carboxyl group is replaced by an $-\text{OR}$ (alkoxy) group.

Amines and Amides: Nitrogen-containing Organics

Many organic compounds contain nitrogen. We encounter a variety of such compounds in the chapters that follow. In this chapter, we introduce two families that will provide you with a vital background for the material ahead—the amines and the amides.

The amines contain the elements carbon, hydrogen, and nitrogen. They are

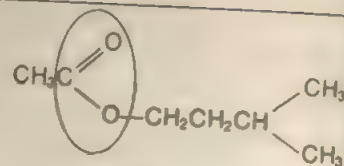




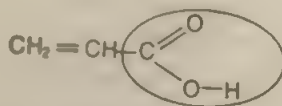
Acetylsalicylic acid
Aspirin



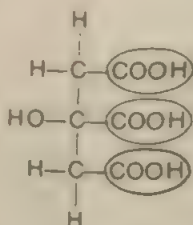
γ -Aminobutyric acid
A powerful depressant



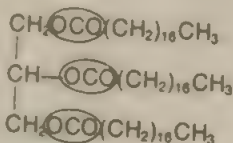
Isoamyl acetate
Banana oil
Used as a solvent and flavoring



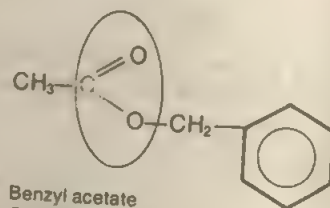
Acrylic acid
Raw material for plastics



Citric acid
Occurs in citrus fruits

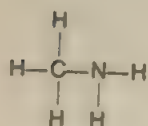


Glycerol tristearate
A fat

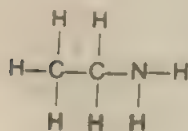


Benzyl acetate
Oil of jasmine
Used in perfumes

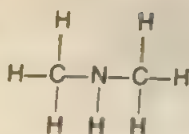
Figure 11.3 Some organic acids and esters of interest.



Methylamine



Ethylamine

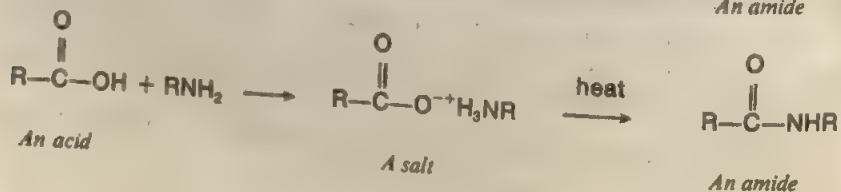
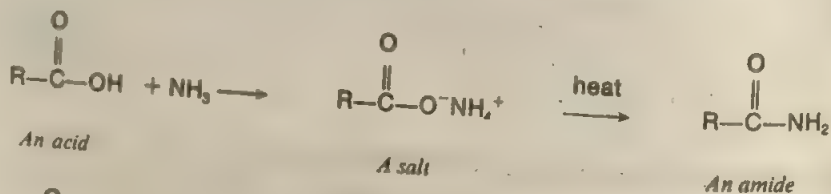


Dimethylamine

derived from ammonia by replacing one, two, or three of the hydrogen atoms by an alkyl (R—) group. The simplest amine has the molecular formula CH_5N . There is only one way these atoms can be put together. (Remember that nitrogen forms three bonds.) The structure of this compound, which is called methylamine, is illustrated, along with those of three other representative amines.

The simple amines are similar to ammonia in odor, basicity, and other properties. It is the higher amines that are the most interesting, though. **Figure 11.4** includes a variety of these. Notice that each structure contains a —NH_2 unit. This is called the *amino group*.

The other nitrogen-containing compounds that we are discussing in this chapter—the amides (what a difference that one letter makes!)—contain oxygen as well as carbon, nitrogen, and hydrogen. Amides can be made by reacting a carboxylic acid with ammonia or an amine to form a salt and then heating the salt to drive off the water.



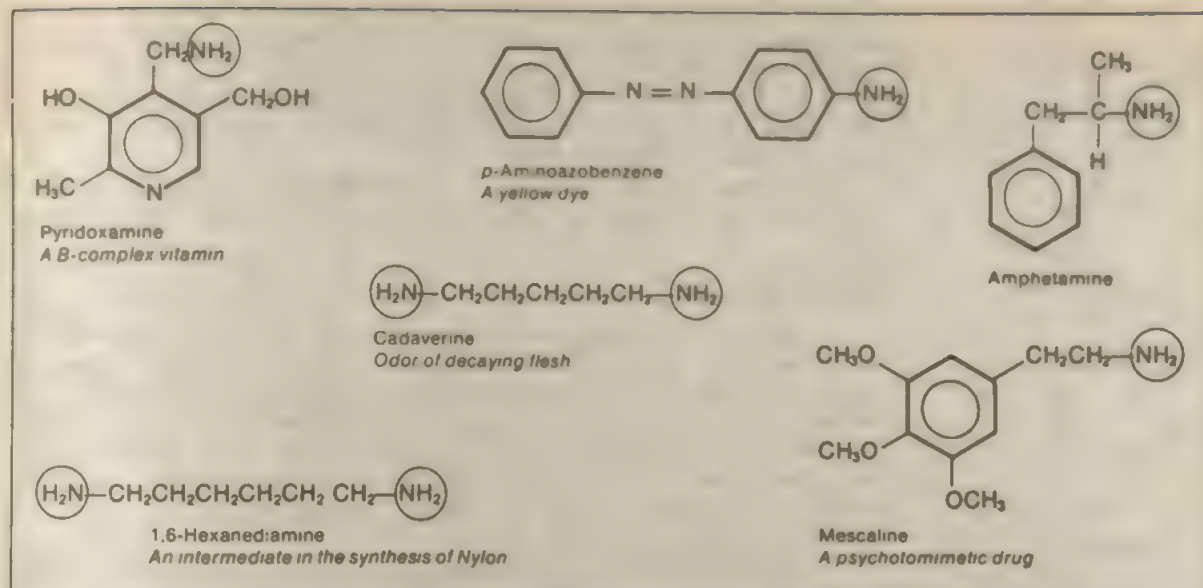
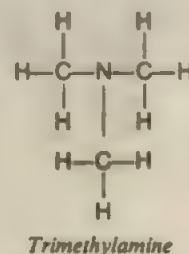


Figure 11.4 Some amines of interest.

The simple amides are of little interest to us here, but the complex amides are of tremendous importance. Nylon (chapter 14) is an amide. Even more important are the proteins (chapter 16), which, quite close to the basis of life itself, are also amides. Remember the amide functional group; you will see it many times in the chapters that follow.

Heterocyclic Compounds: Nitrogen in a Ring

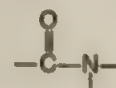
Among the most interesting amines and amides of all are a group of heterocyclic* ones. Four of particular importance are those formed by the breakdown of certain acidic materials found in the nuclei of living cells.



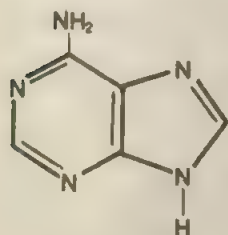
*The ring compounds that we have discussed so far have been, for the most part, rings of carbon atoms. The term *heterocyclic* simply means that the ring contains an atom (or atoms) other than carbon.

Also obtained from these nucleic acids are simple sugars (chapter 16) and phosphoric acid (H_3PO_4).

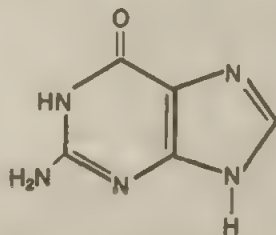
Actually, there are two kinds of nucleic acids. They differ only slightly in composition. Deoxyribonucleic acid (DNA) is composed of the four heterocyclic amines shown here, phosphate, and the simple sugar deoxyribose. Ribonucleic acid (RNA) differs from DNA only in that one base, (thymine) is replaced by uracil and



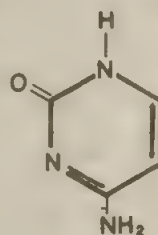
The amide functional group



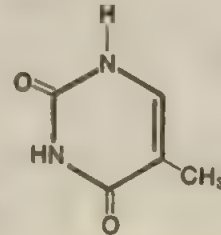
Adenine



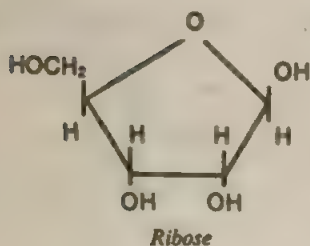
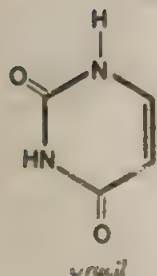
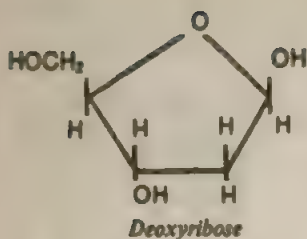
Guanine



Cytosine



Thymine



the sugar (deoxyribose) is replaced by ribose. The two sugars differ by only one oxygen atom.

DNA is the basic hereditary material of all living cells. It can replicate itself. This self-replicating property is the basis of life. Indeed, we might define life in terms of this self-replicating property of DNA.

This master molecule of life, DNA, also controls the production of RNA. RNA in turn controls the production of *proteins* (chapter 16), the building blocks of living cells.

The Double Helix

In 1953, two relative unknowns in the world of science announced that they had worked out the structure of DNA. Using data from X ray studies and working with models not unlike a child's construction set, James D. Watson and Francis Crick determined that DNA must be composed of two helices wound around one another. The phosphate and sugar groups formed the outside of the spiral-staircase arrangement. The heterocyclic amines were paired on the inside, with guanine always joined to cytosine and adenine always connected to thymine. These pairs of bases fit together precisely (figure 11.5).

Watson and Crick received the Nobel Prize for chemistry in 1962 for discovering, as Crick put it, "the secret of life."

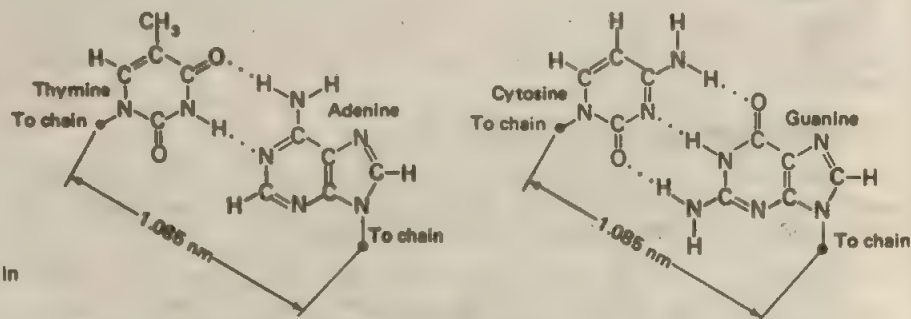


Figure 11.5 The pairing of bases in the DNA double helix.

Nucleic Acids: Self-replication and Protein Synthesis

The structure of DNA is so complex—one molecule can contain millions of atoms—that it often is represented schematically. Figure 11.6a is one such diagram. The "ribbons" represent the sugar-phosphate chains. The heterocyclic amines are represented by their initial letters.

In self-replication, the strands are pulled apart. Each strand then forms a new complementary strand. In this way, two new double helices are formed, each identical to the original.

Although there are only four "letters"—the four bases—in the genetic code, their *sequence* along the strands can vary so widely that they comprise an information storage system that is essentially unlimited. Each cell carries all the information needed to determine all the hereditary characteristics of even the most complex organisms. DNA carries the information for synthesis for all the many kinds of proteins (chapter 16) that carry out the complex functions of living cells. Information (the base sequence) in DNA is transcribed into a complementary strand of RNA. This information is carried to the cellular units called *ribosomes* where proteins are synthesized. The sequence of bases, in groups of three, is translated into a sequence of amino acids in a protein molecule. It is the amino acid *sequence* that

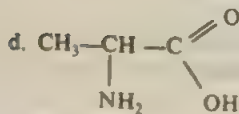
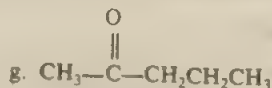
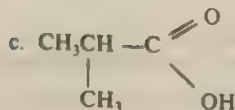
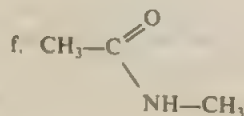
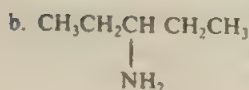
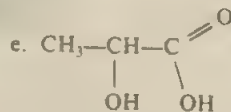
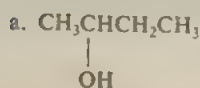
spliced into bacterial or yeast DNA. These microorganisms, grown in huge cultures, may be able to produce large amounts of insulin, thus alleviating a possible shortage. Other important drugs may be produced by similar methods.

Not everyone sees recombinant DNA as an unmixed blessing. Opponents of this genetic manipulation worry about the accidental creation of virulent disease-causing microorganisms against which we have no defenses. This "Andromeda strain," if released, could cause untold death and suffering. The United States National Institute of Health has issued rigid guidelines governing research in recombinant DNA, which are designed to minimize the risk that such accidents may occur.

Recombinant DNA has opened the door to the alteration of our genetic heritage a little wider. The door opens to a new world of promise, and to new perils. We may be able to create a race of giants and geniuses. But who is to decide what sort of creatures we *should* be? Who is to play God with our new secrets of life?

Problems

1. Write structures for each of the following.
 - a. methyl alcohol
 - b. methyl chloride
 - c. methylamine
 - d. ethyl alcohol
 - e. ethyl chloride
 - f. ethylamine
 - g. an amide of formula C_2H_5ON
 - h. the acid of formula $C_3H_6O_2$
 - i. an alcohol of formula C_3H_8O
2. Circle the functional group(s) in each of the following molecules.



3. What is the name of each of the functional groups in problem 2?
4. What are chlorofluorocarbons? How are they used? Should they be used at all?
5. Methanol (from wood or coal) has been proposed as a liquid fuel to replace gasoline. What problems might be involved in its use?
6. Why is ethanol, rather than methanol, used as a solvent for internal medicines?
7. Is ethanol a poison? Explain.
8. Look up (in *The Merck Index*) the LD₅₀ of each of the following.
 - a. acetylsalicylic acid (aspirin)
 - b. ethyl acetate (used as fingernail-polish remover)
 - c. nicotine (occurs to the extent of 2% to 8% in dried leaves of tobacco)

- d. nicotinic acid (a B-complex vitamin)
 - e. morphine (an opiate)
- Are these substances toxic? Explain fully in each case.
9. Describe the Watson-Crick model for DNA. How does the model explain self-replication of genetic material?
 10. Write the equation for the production of ethyl alcohol by the addition of water to ethylene. How much ethyl alcohol can be made from 14 t of ethylene?
 11. Chemical bonds can be broken by ultraviolet radiation, gamma rays, cosmic rays, and certain chemical substances. What are the biological implications of these facts? (Hint: What effect might the breaking of chemical bonds have on DNA?)

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chapter 12

Energy: The Chemical Century

Our modern industrial civilization is fueled by fossils. Over 90% of the energy used to sustain our way of life comes from the fossil fuels—coal, petroleum, and natural gas. The origin of these fossil fuels and their chemical nature were discussed in chapter 10. In this chapter, we consider how these fuels are burned to release chemical energy, energy that was stored ages ago in plants that had captured rays of sunlight.

First, though, let's look at some of the general considerations in energy conversions. Transformations of energy, like changes in matter, are governed by the laws of nature. If you want to understand our current energy problems, you must first learn something of these laws. And you should consider any scheme for energy conversion in the light of these laws—from well or mine to final disposition of waste materials and wasted energy.

Heavenly Sunlight Flooding the Earth with Energy

No doubt you have heard a lot about nuclear energy. Some good things, some not so good. But did you know that life on Earth depends upon nuclear energy? You don't have to worry about problems with the reactor, though. It's about 150 million km away. And it will last, most likely, for another 10 to 15 billion years. That rather ordinary star that we call the sun is the source of nearly all the energy available to us on Earth. The sun is a nuclear fusion reactor that steadily converts hydrogen to helium (chapter 4) with the release of enormous amounts of energy. And, although the Earth receives only about 1 part in 50 billion of that energy, it is abundantly bathed in energy, receiving about 1.73×10^{17} w (173 000 terawatts [Tw])* from the sun.

*The unit of energy in the International System (SI) is the *joule*. A *watt*, the SI unit for power, is 1 joule per second. A 100-w bulb, burning for 1 hour (3600 seconds), would consume 360 000 J of energy. One kilowatt (kw) = 1000 w and 1 Tw = 10^{12} w.

Only small amounts of energy are available to us from other sources. Heat coming up from the Earth's interior amounts to only about 32 Tw, and the tides produce only about 3 Tw. These are almost insignificant quantities; the sun supplies nearly all the energy available in the biosphere. (The biosphere is the thin film of air, water, and soil in which all life exists. It is only about 15 km thick.)

Table 12.1
Rough estimates in the Earth's energy ledger

	Item	Energy (in terawatts)	Approximate Percentages
In	Solar radiation	173 000	99+
	Internal heat	32	0.02
	Tides	3	0.002
		173 035	
Out	Direct reflection	52 000	30
	Direct heating*	81 000	47
	Water cycle*	40 000	23
	Winds*	370	0.2
	Photosynthesis*	40	0.02
		173 410	

Data from M. King Hubbert, "The Energy Resources of the Earth," *Scientific American*, September 1971.

This energy is eventually returned to space via long-wave radiation (heat).



Figure 12.1 The sun is the ultimate source of nearly all our energy. (Courtesy of U.S. Department of Energy.)

Energy and the Life-Support System

Only a small fraction of the energy that the biosphere receives is used in supporting life. In fact, about 30% of the incident radiation is immediately reflected back into space as short-wave radiation (ultraviolet and visible light). Nearly 50% is converted to heat, making the third planet a warm and habitable place. About 23% of the solar radiation is used to power the water cycle (chapter 9), evaporating water from land and seas. The radiant energy of the sun is converted into the potential energy of water vapor, water droplets, and ice crystals in the atmosphere. This potential energy is converted to the kinetic energy of falling rain and snow and of flowing rivers.

A tiny—but most important—fraction of the solar energy is absorbed by green plants, which use it to power photosynthesis. In the presence of green pigments, called *chlorophylls*, this energy is used to convert carbon dioxide and water into glucose, a simple sugar rich in energy (figure 12.2). The glucose can be stored or it can be converted into more complex foods and structural materials. All animals—and nongreen plants such as fungi and bacteria—depend on the stored energy of green plants for survival.

Energy and Chemical Reactions

How fast—or how slowly—chemical reactions take place depends on a number of factors. One such factor is temperature. Reactions generally take place at a faster rate at a higher temperature. For example, coal (carbon) reacts so slowly with

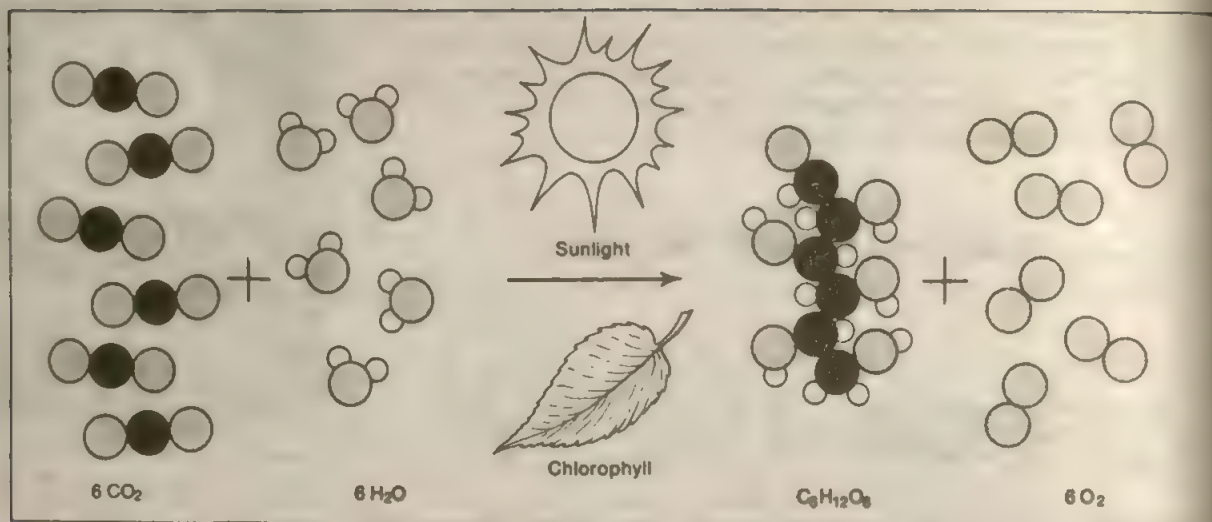


Figure 12.2 Photosynthesis converts carbon dioxide and water into glucose and oxygen.

oxygen (from the air) at room temperature that the change is imperceptible. However, if coal is heated to several hundred degrees, it reacts at a much more rapid rate. The heat evolved in the reaction keeps the coal burning smoothly.

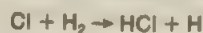
We make use of our knowledge of the temperature effect on chemical reactions in our daily lives. For example, we freeze foods to retard those chemical reactions that lead to spoilage. And, when we want to cook our food more rapidly, we turn up the heat.

The effect of temperature on the rates of chemical reactions is explained in terms of the kinetic-molecular theory. At high temperatures, molecules move more rapidly. Thus, they collide more frequently, creating an increased chance for reaction. The increase in temperature also supplies more energy for the breaking of chemical bonds—a condition necessary for most reactions. For example, in order for hydrogen and chlorine to react, the bonds between hydrogen atoms and between the chlorine atoms must be broken.*

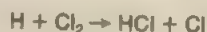
*This statement says nothing about the *order* in which the bonds are broken. The accepted mechanism for the reaction between hydrogen and chlorine is quite complicated. The first step is presumed to be the breaking down of the chlorine molecule into atoms.



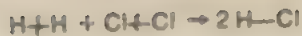
This may be accomplished by absorption of heat or light energy. In the second step, it is postulated that chlorine atoms collide with hydrogen molecules and form hydrogen chloride molecules and hydrogen atoms.



In the third step, it is thought that these hydrogen atoms attack a chlorine molecule and form more HCl and regenerate chlorine atoms.



The second and third steps then are repeated until virtually all the H_2 and Cl_2 are converted to HCl.

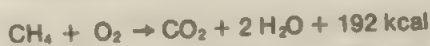


Once the reaction has started, the energy released by the formation of hydrogen to chlorine bonds more than compensates for that required to break the H—H and Cl—Cl bonds, thus, there is a net conversion of chemical energy to heat energy.

Another factor affecting the rate of a chemical reaction is the concentration of reactants. The more molecules there are in a given volume of space, the more likely is a collision. The more collisions there are, the more reactions that occur. For example, you could light a wood splint and then blow out the flame. The splint would continue to glow as the wood reacted slowly with the oxygen of the air. If the glowing splint were placed in pure oxygen, the splint would burst into flame, indicating a much more rapid reaction. This factor can be interpreted in terms of the concentration of oxygen. Air is about 21% oxygen. The concentration of O₂ molecules in pure oxygen is therefore about 5 times as great as in air.

Catalysts also affect the rate of chemical reactions. In chapter 10, we saw how chemists use catalysts to improve the octane rating of gasoline. Catalysts are of great importance in the chemical industry. Reactions that otherwise would be so slow as to be impractical can be made to proceed at a feasible rate with the use of the appropriate catalysts. Catalysts are even more important in living organisms. Biological catalysts, called *enzymes*, mediate nearly all the chemical reactions that take place in living systems. Enzymes are discussed further in subsequent chapters.

The energy changes associated with chemical reactions are quantitatively related to the *amounts* of chemicals that are changed. For example, burning 16 g of methane* to form carbon dioxide and water releases 192 kcal of energy as heat.



Burning 32 g of methane would produce twice as much heat—384 kcal.

Chemical reactions that result in the release of heat are said to be *exothermic*. The burning of methane, gasoline, and coal are all exothermic reactions. In each case, chemical energy is converted into heat energy. There are other reactions, such as the decomposition of water, in which energy must be supplied.

*We did not choose 16 g of methane at random. In chapter 8, we mentioned that 6.02×10^{23} molecules of a substance is a mole of the substance. Obviously, it would be impossible to count that many molecules. Fortunately, counting is also unnecessary. To get a mole of a substance, you merely take the formula weight expressed in grams. (We won't go into just why that is so; if you are interested in the why, you can consult reference 13.) To get the formula weight of a substance, you merely add the atomic weights.

$$\begin{array}{r} 1 \text{ C} = 1 \times 12.0 = 12.0 \\ 4 \text{ H} = 1 \times 1.0 = 4.0 \\ \hline 16.0 \end{array}$$

Thus, the formula weight of methane is 16.0, and a mole of methane is 16.0 g. Similarly, for water, the formula weight is:

$$\begin{array}{r} 1 \text{ O} = 1 \times 16.0 = 16.0 \\ 2 \text{ H} = 2 \times 1.0 = 2.0 \\ \hline 18.0 \end{array}$$

A mole of water is 18.0 g.

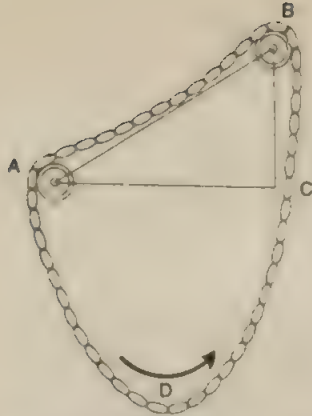
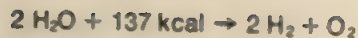
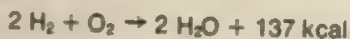


Figure 12.3 A proposed model for perpetual motion. When a uniform chain hangs over two pulleys, the weight of length AD equals the weight of CD. But, since the weight of AB is greater than the weight of BC, the chain should run around in the direction of the arrow, gaining speed and producing energy. But it doesn't. (Reprinted with permission from Stewart, Alec T., *Perpetual Motion: Electrons in Atoms and Crystals*, New York: Doubleday, 1965, p. 2.)



If the energy is supplied as heat, such reactions are said to be *endothermic*. It takes 137 kcal of energy to decompose 36 g of water into hydrogen and oxygen. It should be noted that the same amount of energy is released when enough hydrogen is burned to form 36 g of water.



Keep that in mind when you hear people suggest hydrogen as a possible replacement for natural gas or petroleum as a fuel.

The Energy Enigma: Energy Is Conserved, Yet We're Running Out

We take a look at our present energy sources and our future energy prospects shortly, but, in order to do so scientifically, let's first look at some of the laws of nature. You should recall that natural laws merely summarize the results of many experiments. We won't trouble you with a recounting of all those experiments here, but we'll merely state the laws and some of their consequences.

The *first law of thermodynamics* grew out of a variety of experiments during the early 1800s. By 1840, it was clear that, although it can be changed from one form to another, energy is neither created nor destroyed. This law (also called the *law of conservation of energy*) has been restated in a number of ways, including, "you can't get something for nothing" and "there is no such thing as a free lunch." Energy can't be made from nothing. Neither does it just disappear, although it may go someplace else.

The first law also says that you can't build a "perpetual motion" machine. You can't make a machine that will produce more energy than it consumes. Even if an engine isn't doing any work, it loses energy (as heat) due to the friction of its moving parts. In fact, in any real engine, you can't get as much useful energy as you put in. You can't even break even!

Energy and the Second Law: Things ARE Going to Get Worse

If energy is neither created nor destroyed, why do we always need more? Will what we have now not last forever? The answer lies in the fact that energy can be changed from one form to another and not all forms are equal. And high-grade forms of energy are constantly being degraded into low-grade forms. Energy flows downhill. Mechanical energy eventually is changed into heat energy. Hot objects cool off by transferring their heat to cooler ones. There is a tendency toward an even distribution of energy. Energy always flows from a hot object to a cooler one. The reverse never occurs spontaneously.

Observations of heat flow led to the formulation of the *second law of thermodynamics*. In one form (of many) the law states that energy does not flow spontaneously from a cold object to a hot one. Now it is true that we can *make* energy flow from a cold region to a hot one—that's what refrigerators are all about—but we cannot do so without producing other changes elsewhere. This sort of reversal of a natural process can only be done at a price. The price, in the case of refrigerators, is the consumption of electricity.

Another way to look at the second law is in terms of disorder. Scientists use the term *entropy* to indicate the randomness of a system. The more mixed up it is, the higher the entropy. This concept is illustrated in **figure 12.5**. Natural processes tend toward a greater entropy—toward disorder.

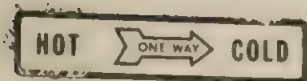


Figure 12.4 Energy always flows spontaneously from hot to cold, never the reverse.



Figure 12.5 Any spontaneous change is toward a less ordered state—toward greater entropy.

The nursery rhyme "Humpty-Dumpty" illustrates the second law. Once Humpty had fallen and been broken into a more disordered state, "all the king's horses and all the king's men" couldn't put him together again. Once we have taken all the high-grade iron ore (highly ordered iron atoms) and distributed it throughout the world as particles of rust (randomly distributed iron atoms), all the world's geologists and all the world's chemists won't be able to put them together again.

Actually, we sometimes can reverse the tendency toward randomness but only through the expenditure of energy. For example, a new deck of playing cards could be arranged by suit and by rank, a situation of high order (low entropy). If the cards were dropped and scattered randomly about the floor (higher entropy), they could be returned to their ordered state only by the expenditure of energy—bending, stooping, and stacking. Your body would have to convert food energy to muscular energy to do the task. It is quite unlikely that the cards would pick themselves up off the floor and resume their ordered state.

The second law places some restrictions on what can be done. It also has something to say about what we should do about many of our environmental problems, and it points out rather firmly a number of things that we cannot do.

Entropy and the End of Everything

The second law is supported by innumerable scientific experiments and observations. It is thought to be valid throughout the universe. Thus, the laws of thermodynamics give us some insight into the future of the universe. Although the first law states that energy is conserved, the second law tells us that energy flows downhill toward less useful forms. In every spontaneous process, some energy is converted to low-grade heat. This energy can do no useful work; it only warms the universe a tiny amount. The entropy of the universe tends always toward a maximum. When that maximum is reached, energy will have been evenly spread throughout the universe. All objects in the universe will be at the same uniform low temperature. The universe will have "wound down." Life will have ceased long before this state is reached. The only motion left in this hostile environment will be the gentle vibration of atoms.

The second law tells us that the end of the universe is inevitable, but that fact need not concern us too much. The end is billions of years away, and we have energy problems right now. With the laws of thermodynamics in mind, let's put our present problems in perspective through a brief look at the history of the way humans have used energy so far.

People Power: Early Uses of Energy

Primitive peoples obtained their energy (food and fuel) by collecting wild plants and hunting wild animals. They expended the energy so obtained in hunting and gathering. Domestication of the horse and the ox increased the availability of energy only slightly. The raw materials used by these work animals were natural—and replaceable—plant materials.

Probably the first device used to convert energy into useful work was the waterwheel. The Egyptians first used waterpower about 2000 years ago, primarily for grinding grain. Later on, waterpower was used for sawmills, textile mills, and other small factories.

Windmills were introduced into western Europe during the Middle Ages. Windpower was used for pumping water, grinding grain, and (more recently) generating electricity.

Windmills and waterwheels are fairly simple devices for converting the kinetic energy of blowing wind and flowing water into mechanical energy. These were

sufficient to power the early part of the industrial revolution, but it was the development of the steam engine that freed the factories from the necessity of being located along waterways. Since 1850, the water turbine, the internal combustion engine, the steam turbine, the gas turbine, and a variety of other energy-conversion devices have been added to the arsenal. In fact, it has been estimated that the power output of all these conversion devices has increased by a factor of 10 000!

The Fossil Fuel Feast: A Brief Interlude

After the steam engine came into widespread use (by about 1850), the industrial revolution was powered largely by coal. By 1900, about 95% of the world's energy production came from burning coal. With the development of the internal combustion engine, petroleum became increasingly important and by 1950 had replaced coal as the principal fuel.

The supply of fossil fuels on the Earth is limited. Estimated United States and world reserves are given in **Table 12.2**. We burn these materials at a rapid and ever-increasing rate. Annual United States and world production are given in **Table 12.3**.

Estimates of reserves can vary a great deal, depending on the assumptions being made. Even the most optimistic estimates, however, lead to the conclusion that the nonrenewable energy resources are being depleted rapidly. Indeed, in just a century, we will have used up over half the fossil fuels that were formed over the ages. As far as energy sources are concerned, we are in the midst of the "chemical century" (reference 14).

Table 12.2
Estimated United States and world reserves of economically recoverable fuels*

<i>Fuel</i>	<i>United States</i>	<i>World</i>
Coal	158 725 000 000	430 101 000 000
Petroleum	6 805 000 000	111 029 000 000
Natural gas	8 944 000 000	78 848 000 000

Data from Department of Economic and Social Affairs, *Statistical Yearbook 1975*, New York: United Nations, 1976.

*All figures are expressed in metric tons of coal equivalents for ready comparison of energy content. One metric ton of crude petroleum is equivalent to 1.47 t of coal. For natural gas, 1000 m³ is equivalent to 1.332 t of coal. Coal reserves do not include lignite (brown coal).

Table 12.3
Annual United States and world production of fossil fuels
in metric tons of coal equivalents.

<i>Fuel</i>	<i>United States</i>	<i>World</i>
Coal	539 000 000	2 227 000 000
Petroleum	637 000 000	4 104 000 000
Natural gas	782 000 000	1 672 000 000

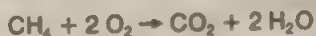
Data from Department of Economic and Social Affairs, *Statistical Yearbook 1975*, New York: United Nations, 1976.

Natural Gas: Clean but Scarce

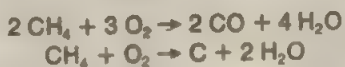
Natural gas is the nicest of the fossil fuels. It can contain a variety of impurities as it comes from the ground, but most of its obnoxious impurities can be removed by

processing. As a gas, it flows through pipes to wherever it is needed. Only an occasional boost from a pumping station is needed. Very little of its energy is needed to get natural gas from the ground to the consumer.

Recall (from chapter 10) that natural gas is composed mainly of methane. It burns with a relatively clean flame, and the products are mainly carbon dioxide and water.



As in any combustion in air, some nitrogen oxides are formed. The role of these compounds in air pollution is discussed in chapter 19. When natural gas is burned in limited amounts of air, carbon monoxide or even elemental carbon (soot) can be major products.



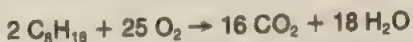
Even so, natural gas is the cleanest of the fossil fuels. Unfortunately, it is also the fuel in shortest supply. Our reserves are expected to decline over the next 30 years or so. After the turn of the century, natural gas probably will contribute little to our energy budget.

Petroleum: What There Is Isn't All Ours

Petroleum is more abundant than natural gas. It also contains more impurities. Some of the impurities can be removed by processing, but petroleum-derived fuels are generally dirtier than natural gas. Crude oil is liquid, a most convenient form for transporting it. Petroleum is pumped easily through pipelines or hauled across the oceans in giant tankers. Little energy is required to pump petroleum from the ground. As domestic supplies diminish, though, we will have to expend an increasing fraction of the energy content of petroleum to transport it to where it is needed. Also, as petroleum is pumped out of a well, the petroleum that remains behind is increasingly difficult to get out. This is a natural consequence of the second law of thermodynamics: that which is left behind is more scattered and more energy is required to collect it.

The Earth's supply of petroleum probably will last a little longer than its supply of natural gas. United States petroleum reserves are expected to decline rapidly. Even the massive field on the North Slope of Alaska would last only 2 or 3 years if it were our only source. Offshore deposits along the Atlantic coast of the United States would produce only a few years' supply, and offshore drilling requires a great deal more energy (and money) than drilling on land. We now import about 50% of our petroleum. Our continued dependence on petroleum will force us to import even more oil. This will make our balance-of-payments problems even worse and increase other international economic problems as well.

Recall (from chapter 10) that petroleum is largely a mixture of hydrocarbons. Hydrocarbons burn readily. Complete combustion yields mainly carbon dioxide and water. A representative reaction is that of an octane.



Combustion in air also leads to the formation of nitrogen oxides. Incomplete burning produces carbon monoxide and soot. Petroleum usually contains small amounts of sulfur compounds that produce sulfur dioxide when burned.

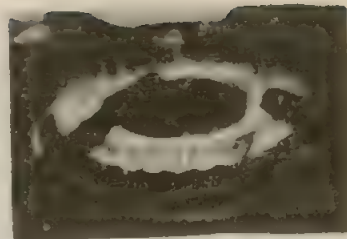


Figure 12.6 Natural gas burns with a relatively clean flame. Unfortunately, it is in short supply. (Courtesy of the American Gas Association.)

Figure 12.7 Petroleum can be burned rather cleanly to heat homes or in power plants to produce electricity. Most of it, however, is burned in internal combustion engines to propel automobiles. These inefficient machines contribute mightily to air pollution.



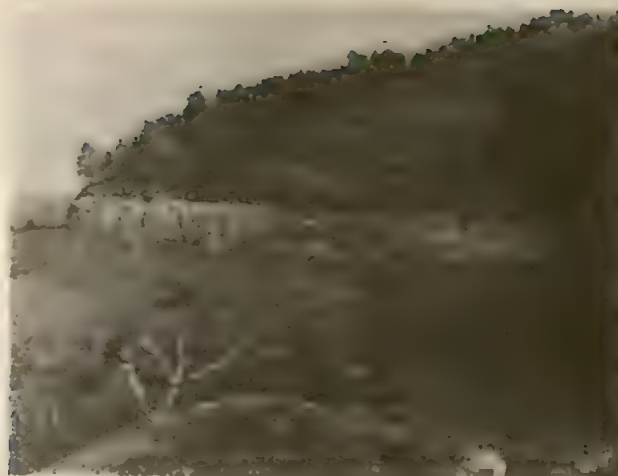
Efficiently burned, petroleum products are rather clean fuels. Fuel oil, used for heating homes or burned to produce electricity, can be burned efficiently while contributing only moderately to air pollution. Gasoline, however, is the major fraction of petroleum. This fuel is used to power automobiles, and the internal combustion engines in most automobiles are highly inefficient and contribute heavily to air pollution (chapter 19).

Air pollution isn't our only problem. Petroleum isn't used only for fuel. Nearly all our industrial organic chemicals come from petroleum (smaller amounts are derived from coal and natural gas). Plastics, synthetic fibers, solvents, and many other consumer products are made from chemicals derived from petroleum. Burning up our petroleum reserves will leave us without a ready source of many familiar materials.

Coal: Dirty, Inconvenient, and Invaluable

Coal is an inconvenient fuel. As a solid, it can't be pumped through pipes to get it out of the ground. It must be removed by dangerous deep-mining or devastating strip-mining. It may be possible to transport coal by grinding it to a powder, mixing it with water, and pumping the slurry through a pipeline. At the present time, though, coal has to be hauled by trucks, trains, and barges. A good deal of energy is consumed in getting coal from the mine to the power plant or the factory where it is to be used.

Coal is our most plentiful fossil fuel. The United States is estimated to have 33% of the world's reserves of coal. There is probably enough easily recoverable coal to last us several hundred years. Unfortunately, the use of coal is associated with some of our worst environmental problems. It can be obtained most inexpensively by strip-mining. Vast areas are ripped bare of all vegetation, and the exposed soil washes away, filling streams with mud and silt. Stripped areas sometimes can be restored, but restoration is expensive. Laws in the United States now require the restoration of most stripped areas and ban stripping on steep slopes where



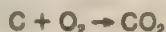
(a)



(b)

restoration is not feasible. Unfortunately, a lot of damage was done before the laws were passed, and many conservationists still consider the present laws inadequate.

The fuel value of coal depends largely on its carbon content. Complete combustion of the carbon produces carbon dioxide.



But in limited amounts of air, large quantities of carbon monoxide and soot are formed.



The soot is mostly unburned carbon.

Coal, a solid, contains a wide variety of impurities. Unlike natural gas and petroleum, coal often contains a lot of minerals. When the coal is burned, the minerals are left as *fly ash*, which presents a major solid-waste disposal problem. Some minerals enter the air as *particulate matter*, constituting a major pollution problem.

Perhaps even worse, most of our remaining coal is high in sulfur. When it burns, choking sulfur dioxide is poured into the atmosphere. Reacting with oxygen and moisture in the air, the sulfur dioxide is converted into sulfuric acid. This acid slowly eats away steel and aluminum structures, marble buildings and statues, and human lungs. The contribution of coal-burning to air pollution is discussed further in chapter 19.

There are ways to clean up coal before it is burned, and coal also can be converted to more convenient gaseous and liquid fuels. These processes and other future fuel sources are discussed in the next chapter. Perhaps one or more of these processes will supply most of our energy in the twenty-first century. For many years to come, though, coal—dirty and inconvenient as it is—will remain our best hope for abundant energy.

Problems

1. Write equations for the complete combustion of each of the following.

a. coal (carbon)

b. natural gas (methane)

c. a typical petroleum hydrocarbon

Figure 12.8 The site of a strip mine in Morgan County, Tennessee. (a) The abandoned mine in 1963. (b) The same mine after it was reclaimed in a demonstration project, 1971. (Courtesy of the Tennessee Valley Authority Information Office, Knoxville, Tenn.)

2. Write equations for the incomplete combustion that forms carbon monoxide from each of the substances in problem 1.
3. What are the advantages and the disadvantages of each of the fossil fuels?
4. Living organisms seem to violate the second law of thermodynamics in that they take materials from a less ordered to a more ordered state. How are they able to do that?
5. Can fossil fuels be recycled? If your answer is yes, explain how. If your answer is no, explain why not.
6. What is the ultimate source of nearly all the energy on Earth?
7. State the first law of thermodynamics. How can we ever run short of energy if this law is valid?
8. State the second law of thermodynamics in terms of energy flow and in terms of order and disorder. Does entropy increase or decrease when a fossil fuel is burned?
9. List three factors that influence the rates of chemical reactions.
10. Why did the United States shift from coal to petroleum and natural gas when we have much larger reserves of coal than of the two hydrocarbons?

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chapter 13

Energy for the Future: After Fossil and Fissile Fuels Fizzle

Within your lifetime, it is likely that natural gas and petroleum will become so scarce and so expensive that people won't be able to afford to burn them as fuels. Coal, too, will become more expensive as readily mined deposits are removed. We can obtain energy from nuclear fission (chapter 4), but the supply of natural fissile fuels is also quite limited. What then?

In this chapter, we consider a variety of energy sources, some of them that will supplement fossil fuels for now and others that will contribute to our energy needs in the future. One or more of the sources may well replace fossil fuels as our source of energy as the "chemical century" draws to a close.

Nuclear Power: Paradise or Perdition?

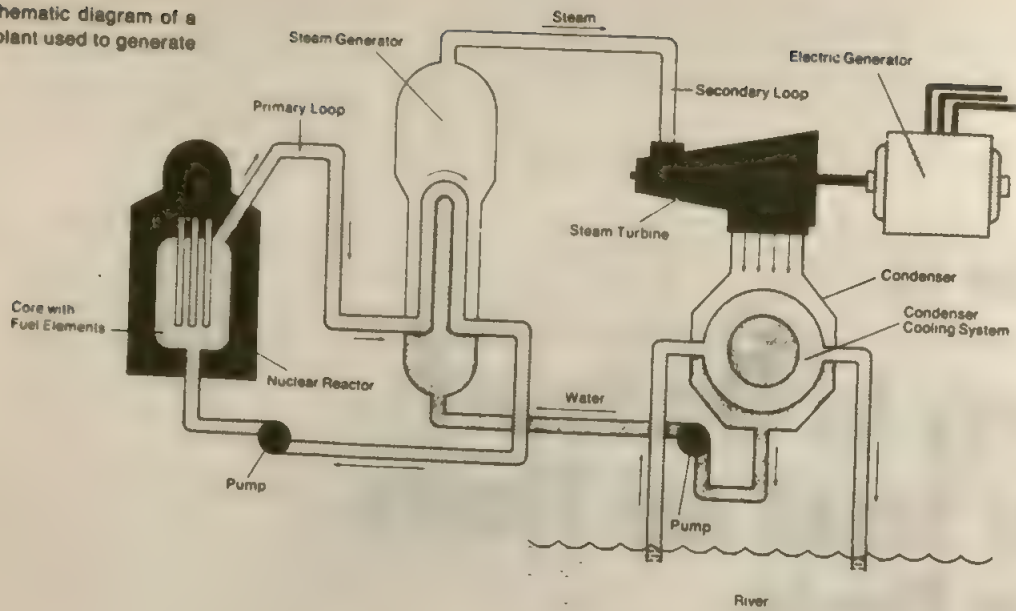
The fission reactions that power nuclear bombs can be controlled in nuclear reactors. The energy released during fission can be used to generate steam, and the steam can turn a turbine, thus generating electricity (figure 13.1).

In 1978, about 2% of United States energy came from nuclear power. However, nuclear power plants accounted for about 10% of the electricity generated. By 1985, 25% of our electricity may come from nuclear fission. Even now, the eastern seaboard and upper midwestern states, many of which have little fossil fuel reserves, are heavily dependent on nuclear power for electricity.

There are actually several types of nuclear power plants. The one diagrammed in figure 13.1 is a pressurized water reactor, the principal type now being constructed in the United States. Earlier models were mainly boiling water reactors in which the steam from the reactor was used to power the turbine directly. No attempt is made here to discuss all the possible types of reactors. However, a summary of the characteristics of several types is provided in table 13.1.

At the dawn of the nuclear age, nuclear power was envisioned by some to be destined to fulfill the Biblical prophecy of a fiery end to our world. Indeed, as the cold war between the United States and the Union of Soviet Socialist Republics

Figure 13.1 Schematic diagram of a nuclear power plant used to generate electricity.



intensified during the 1950s, it was difficult to see how nuclear war could be avoided. If it had come, it could well have been the end of life on Earth.

While some were predicting doom, others saw nuclear power as a source of unlimited energy. During the late 1940s, it was commonly predicted that electricity from nuclear plants would be so cheap eventually that it would not have to be metered. Lights in public buildings could be left on continuously; on-off switches would not be needed!

Obviously, nuclear power has not yet brought us either paradise or perdition. It has become, however, one of the most controversial issues of our time. Our great need for energy indicates that the controversy will continue for years to come.

Nuclear power plants use the same fission reactions as nuclear bombs. A

Table 13.1
Characteristics of several types of nuclear reactors

Reactor	Abbreviation	Fuel	Moderator	Primary Coolant	Fluid in Secondary Loop
Light water	LWR				
Boiling water	BWR	^{235}U (enriched to 3%)	Water	Water	(No secondary loop)
Pressurized water	PWR	^{235}U (enriched to 3%)	Water	Water	Water
Canadian uranium-deuterium	CANDU	^{235}U (natural abundance)	Heavy water*	Heavy water	Water
High-temperature gas-cooled	HTGR	^{235}U (enriched to 3%)	Graphite	Helium gas	Water
Liquid-metal fast breeder	LMFBR	^{235}U (at start), then ^{238}U converted to ^{239}Pu	—	Molten sodium	Molten sodium†

*Heavy water is water enriched with the heavy isotope of hydrogen called deuterium (^2_1H). Heavy water often is indicated by the formula D_2O . Other references to water are to ordinary, or light, water.
†A third loop in the LMFBR contains water, which is converted to steam to power the turbine.

moderator (table 13.1) is used to slow down the fission neutrons. Also, the reaction is controlled by the insertion of boron steel or cadmium control rods. Boron and cadmium absorb neutrons readily, so the rods prevent the neutrons from participating in the chain reaction. These rods are installed as the reactor is built. Removing them part way starts the chain reaction; the reaction is stopped when the rods are pushed all the way in.

The tremendous heat of the nuclear reaction is used to produce steam. In turn, the steam is used to turn turbines, which generate electricity (figure 13.1). Nuclear power plants have one great advantage over coal- and oil-burning plants—they do not pollute the air with soot, fly ash, sulfur dioxide, or other noxious chemicals. However, nuclear plants offer some disadvantages as well. First, the reactor requires heavy shielding to protect its operators from radiation. Second, fissionable fuel is rare and expensive. It is estimated that the supply of high-grade (easily obtained) uranium ore will run out by the year 2000. Third, the radioactive fission products present a serious disposal problem. Putting them in deep wells or mines or burying them at sea is like sweeping them under a rug. Do we have the right to leave our descendants with a problem that they will have to contend with for 250 000 years? Fourth, the waste heat from the generating plants heats up the environment. This effect is known as *thermal pollution*. Nuclear plants produce more waste heat than fossil fuel plants of the same capacity. Fifth, no matter how carefully they are constructed, nuclear plants release some radioactivity into the surrounding environment. Although proponents of nuclear power say that the amount is negligible, others say that *any* increase in radiation exposure is dangerous. Sixth, there is the possibility of a major accident at a reactor site. Such an accident could release large amounts of radioactivity into the surrounding countryside.

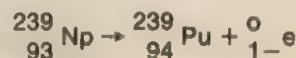
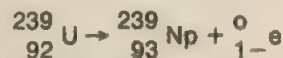
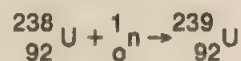
In 1979, an accident at the Three Mile Island nuclear power plant near Harrisburg, Pennsylvania, released small amounts of radioactivity into the environment. Although no one was killed or seriously injured, this accident whetted the public's fears of nuclear power. And none of us will know for many years what the long-term effects of that accident—or any exposure to low-level radiation—will be. Only time will tell whether there will be increased deaths from cancer, or birth defects in children of parents exposed to that radiation.

Uranium-fueled power plants cannot explode like nuclear bombs, as some opponents of nuclear power seem to fear that they could. The uranium is enriched to at most 3% or 4% uranium-235. To make a bomb, you need about 90% uranium-235.

There is considerable controversy over most aspects of nuclear power, and there are scientists on both sides. While they may be able to agree on the results of laboratory experiments, scientists obviously do not agree on what is best for society. Those who wish to explore this controversy further are urged to see the references and readings at the end of this chapter.

Breeder Reactors: Making More Fuel Than We Burn

Less than 1% of naturally occurring uranium is the fissionable uranium-235 isotope. Large quantities of uranium-238 are available as a by-product of the production of uranium-235. Uranium-238 can be converted to fissile plutonium-239 by bombardment with neutrons. Uranium-239 is formed initially, but it rapidly decays to neptunium-239. The neptunium quickly decays to plutonium. The reactions are shown in the margin. A reactor can be built with a core of fissionable plutonium surrounded by uranium-238. As the plutonium fissions, neutrons convert the uranium-238 shield to more plutonium; thus, the reactor breeds more fuel than it consumes. There is enough uranium-238 to last several centuries, so one of the disadvantages of nuclear plants could be overcome by the use of breeder reactors.



Plutonium-breeding reactions

Breeder reactors have some problems of their own, however. Plutonium is fairly low-melting (640 °C), and the plant is limited to fairly cool—and inefficient—operation. Water is not adequate as a coolant; it is necessary to use molten sodium metal in the primary loop. These reactors often are called liquid-metal fast breeder reactors (LMFBR). Should an accident occur in such a breeder, the sodium could react violently with both the water and air.

Since plutonium is low-melting, a failure of the cooling system could cause the reactor's core to melt. The radioactive fission products and the plutonium could be released into the environment, with devastating effects. All reactors are required to have an emergency backup core-cooling system. Whether these systems work or not is one of the principal areas of controversy.

Spokespeople for the nuclear power industry claim that the industry has an outstanding record for safety. They contend that their reactors are designed so that they are fail-safe. The industry's critics counter that nuclear accidents may well be only a remote possibility but that any major accident would be an utter catastrophe. Thousands of people might be killed immediately and millions more condemned to a slow death from radiation poisoning. Huge areas might be rendered uninhabitable for centuries.

Plutonium is highly toxic. It emits alpha particles and this property makes it especially dangerous when it is ingested. It is estimated that 1 microgram (μg) in the lungs of a human is enough to induce lung cancer.

A further hazard is that reactor-grade plutonium, unlike the uranium used in nuclear reactors, could be readily converted into a nuclear bomb. The use of plutonium as a reactor fuel could easily lead to the further spread of nuclear weapons. There is even the possibility that terrorist groups could fashion a crude weapon from stolen plutonium. They then could threaten to destroy an entire city in order to force the authorities into meeting their demands.

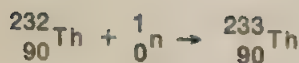
Plutonium is produced for nuclear weapons. Some plutonium is formed in ordinary (nonbreeder) reactors. Plutonium has a half-life of about 25 000 years. Assuming that it will be essentially gone after 10 half-lives, we can estimate that our descendants would have to contend with plutonium for 250 000 years.

Another possible breeder reaction is that in which thorium-232 is converted to fissile uranium-233. It is thought that it would be rather difficult to make bombs from reactor-grade uranium-233. However, uranium-233 is like plutonium in that it emits damaging alpha particles. And it has an even longer half-life—160 000 years.

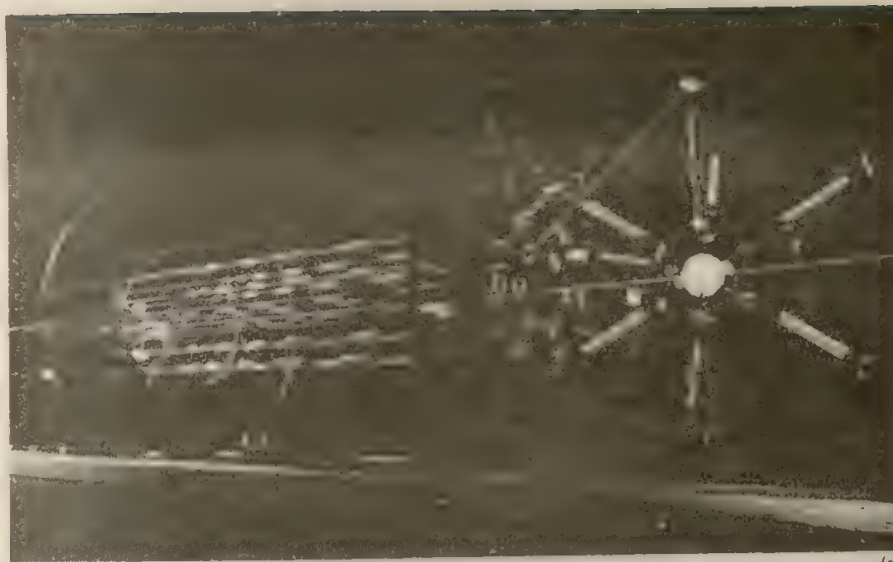
The breeder reactor may be an important power source for the future but not before some substantial technical problems have been overcome. To date, our experience with breeder reactors has not been too encouraging. One such plant near Detroit was closed permanently in 1972 after producing very little electricity. The next breeder, scheduled to be built on the Clinch River in Tennessee, has been delayed, perhaps for years. Even if the project is speeded up, the plant is not expected to produce electricity until the middle or late 1980s. It is unlikely that the breeder reactor, if it were developed, would contribute very much to the United States energy supply before the twenty-first century. European nations, however, are moving ahead rapidly with the development of breeder reactors.

Nuclear Fusion: The Sun in a Magnetic Bottle

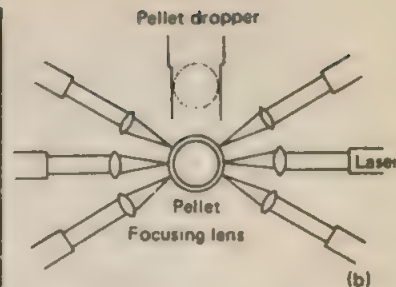
In chapter 4, we discussed the thermonuclear reactions that power the sun and that have been adapted by scientists and engineers for making hydrogen bombs. If we could find some way to control these fusion reactions and use them to produce electricity, we would have a nearly unlimited source of power. To date, the fusion reactions are useful only for the making of bombs, although research in the control



Uranium-233-breeding reactions



(a)



(b)

Figure 13.2 Sharply focused laser beams may be used someday to initiate nuclear fusion. (a) A model of the 10 000-J high-energy laser with which scientists hope to achieve fusion. (b) How laser energy may be used to compress and heat rapidly a small pellet containing deuterium and tritium; the great heat and pressure applied almost instantaneously cause the nuclei to fuse. (Photo courtesy of the Lawrence Livermore Laboratory, Berkeley, Calif.)

of nuclear fusion is progressing. Controlled fusion would have several advantages over the nuclear fission reactors. The principal fuel, deuterium (${}^2\text{H}$), is plentiful and is obtained easily by the fractional electrolysis (splitting apart by means of electricity) of water, even though only 1 hydrogen atom in 5000 is a deuterium atom. (We have oceans full of water to work with.) The problem of radioactive wastes would be minimized. The end product—helium—is stable and biologically inert. Escape of tritium might be a problem, because this hydrogen isotope would be readily incorporated into organisms. Tritium (${}^3\text{H}$) undergoes beta decay, with a half-life of 12.3 years. And there is one other problem associated with any production and use of energy: the unavoidable loss of part of the energy as heat. We would still have to be concerned with thermal pollution.

Great technical difficulties would have to be overcome before a controlled fusion reaction could be used in the production of energy. Temperatures of 50 000 000 °C would have to be attained, and no material on Earth could withstand more than a few thousand degrees. At a temperature of 50 000 000 °C, no molecule could hold together, nor could the atoms from which molecules are made. All atoms would be stripped of their electrons, and the nuclei and free electrons would form a mixture called a *plasma* (no relation to blood plasma). There is hope that this plasma could be contained by a strong magnetic field. Scientists in several nations are getting closer to the development of the environment necessary for controlled fusion.

Nuclear fusion may well be our best hope for relatively clean, abundant energy in the future. Much work remains to be done, however. Even when controlled fusion is achieved in the laboratory, it will still be a long time before it becomes a practical source of energy. A prototype power plant will have to be built and tested. If it were successful, commercial plants then could be constructed. It is unlikely that we will get any significant energy from controlled fusion until well into the next century.

Harnessing the Sun: Solar Energy

At the beginning of chapter 12, we saw that nearly all the energy on the Earth comes from the sun. With all that energy from our celestial power plant, why do we face an energy crisis? The answer lies in the fact that this energy is thinly spread and difficult to concentrate.

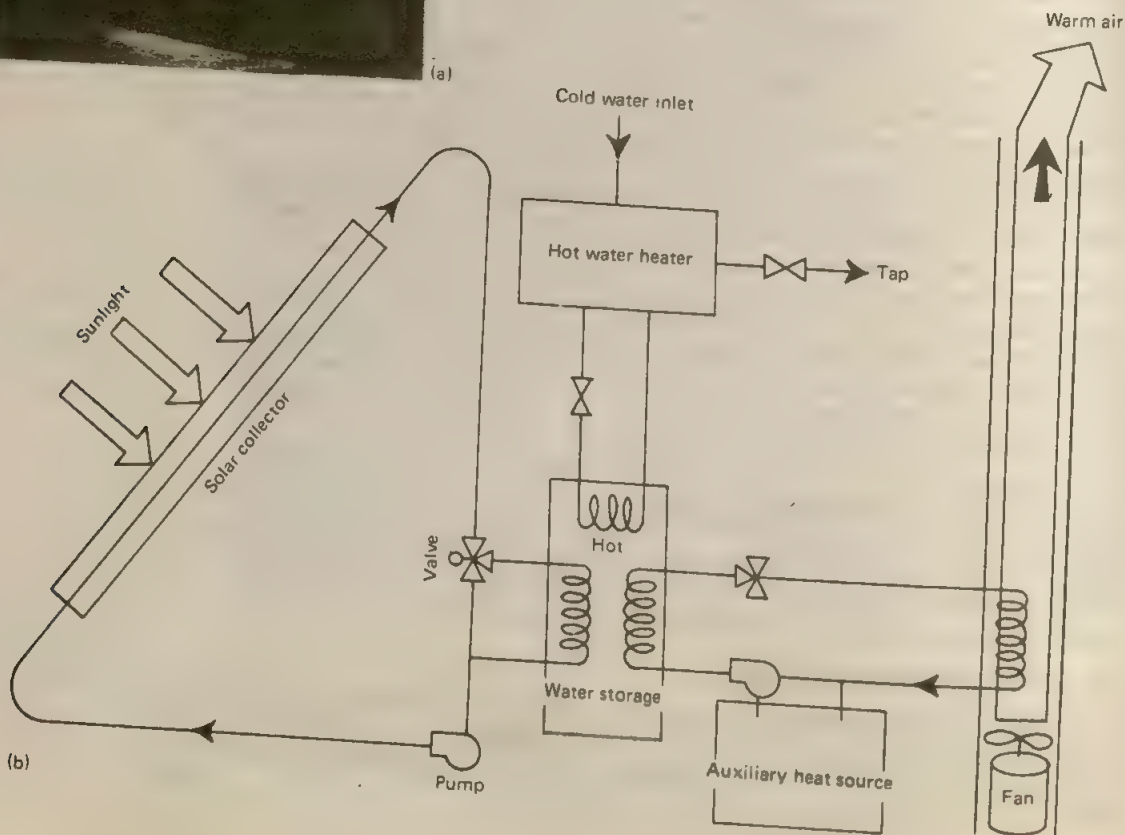
Diffuse energy is not very useful. As it arrives on the surface of the Earth, about 50% of the solar energy is converted to heat. Another 30% is simply reflected back into space. We can increase the efficiency of this conversion rather easily. A black surface absorbs radiation better than colored ones. A simple solar collector can be made by covering a metal surface, painted black, with a glass plate. The glass is transparent to the incoming solar radiation, but it partially prevents the heat from escaping back into space. The hot surface is used to heat water or other fluids, and the hot fluids usually are stored in an insulated tank. Water, heated in this manner, can be used directly for bathing, dish washing, laundry, and such. To heat a building, air can be warmed by being passed around the reservoir and then circulated through the building. Even in the cold northern climates, about 50% of the home heating requirements could be met by solar collectors. These installations are expensive but would pay for themselves, through fuel savings, in 10 years—or less, if the costs of heating fuels continued to rise.

14



(a)

Figure 13.3 (a) "Solar One," an experimental house designed by the University of Delaware's Institute of Energy Conversion; the house obtains about 80% of its energy requirement from the sun. (b) A diagram of a solar collector that furnishes hot water and warm-air heat. (Photo courtesy of the University of Delaware.)



In hot climates, solar energy can be used to provide air conditioning. That may seem paradoxical, but it really isn't. All air conditioners require a source of energy. Most use electricity, but devices powered by natural gas have been used for years. Solar air conditioners operate in a similar manner; sunlight is concentrated to produce the energy (heat) required to drive the compressor.

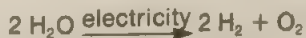
Sunlight also can be converted directly to electricity by devices called *photovoltaic cells* or, more simply, *solar cells*. These devices can be made from a variety of substances, but the most common are made from elemental silicon. In a crystal of pure silicon, each silicon atom has four valence electrons and is covalently bonded to four other silicon atoms (**figure 13.4**). In the manufacture of a solar cell, extremely pure silicon is doped with small amounts of specific impurities and formed into single crystals. One type of crystal has about 1 part per million (ppm) of arsenic added. Arsenic atoms have five valence electrons, four of which are used to form bonds to silicon atoms. The fifth electron is relatively free to move around. This type of crystal, with extra electrons, is called the *donor*. Another crystal is made by adding about 1 ppm of boron. Boron atoms have three valence electrons, but there is a shortage of one electron, leaving a *positive hole* in the crystal. This boron-doped crystal is called the *acceptor*.

When the two types of crystals are joined, there is a strong tendency for electrons to flow from the donor to the acceptor. However, the holes near the junction are quickly filled by nearby mobile electrons, and the flow ceases. When sunlight strikes the cell, more electrons are dislodged, creating more mobile electrons and more positive holes. When the two crystals are connected by an external circuit, electrons flow from the donor to the acceptor (**figure 13.5**).

An array of solar cells can be combined to form a solar battery. Such solar batteries can produce about 100 w per square metre of surface; it takes a square metre of cells to power one 100-w light bulb.

Solar batteries have been used for years to power spaceships. They are now being used to provide electricity for weather instruments in remote areas. Unfortunately, they are too expensive for general use. Solar cells are not very efficient, either. Much of the sunlight striking them is reflected back into space. Their present efficiency of conversion is only about 10%. Generation of enough energy to meet a significant portion of our demands would require covering vast areas of desert land with solar cells. It would require 2000 hectares (ha), or about 5000 acres, of cloud-free desert land to produce as much energy as one nuclear power plant. Research is underway to increase the efficiency of solar cells. It is hoped that an efficiency of about 20% can be attained, thus reducing the land area required by 50%.

Using solar energy would require the storage of energy for use at night and on cloudy days. One scheme would involve storage of energy as heat. While the sun shone, energy would be transferred to tanks of molten salts. Then, heat from these salts could, as needed, be used to generate steam to run a turbine, which would generate electricity. Another possibility is using electricity generated during hours of sunshine to electrolyze water to hydrogen and oxygen.



The hydrogen could be transported in tanks or through pipelines (much as natural gas is today) to be used as fuel when and where it was needed. It also could be burned at night to generate electricity.

The technology is available now for the use of solar energy for space heating and for providing hot water. Electricity from solar energy is probably several years away. More research and development are needed.

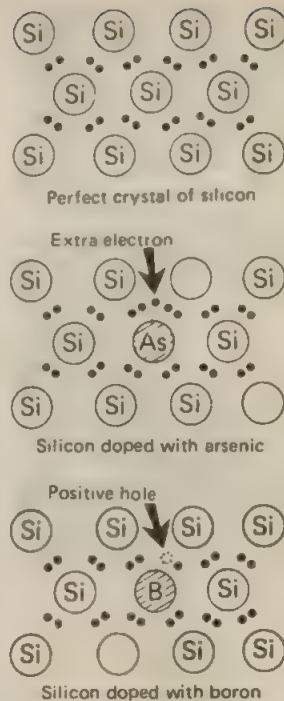


Figure 13.4 Models of silicon crystals. The crystals doped with impurities are used in solar cells.

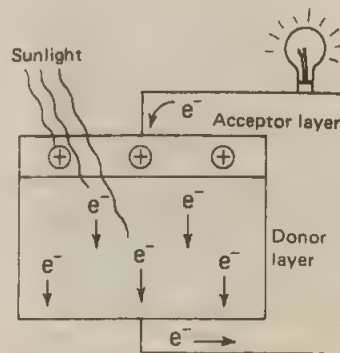


Figure 13.5 Schematic diagram of a solar cell. Electrons flow from the donor crystal to the acceptor crystal through the external circuit.

Biomass: Photosynthesis for Fuel

Why bother with solar collectors and photovoltaic cells to capture energy from the sun when green plants do it every day? Indeed, the idea of growing plants and burning them for energy has been explored. Dry plant material burns quite well. It could be used to fuel a power plant for the generation of electricity. We could start "energy plantations" to grow plants for use as fuel. Burning this *biomass* has some nice advantages: it is a renewable resource whose production is powered by the sun (figure 13.6).

Unfortunately, there are a number of disadvantages to this scheme, too. Most of the available land is needed for the production of food. Even where productive land is available, there are problems. The plants have to be planted, harvested, and hauled to the power plant. Often, the available land is far from where the energy is needed. And the overall efficiency is even less than that of solar cells, only about 3% at best.

The plant material need not be burned directly. Plants high in starches and sugars can be fermented to form ethyl alcohol. Wood can be distilled in the absence of air to produce methyl alcohol (chapter 11). Both alcohols are liquids; this makes them convenient to transport. Both are also excellent fuels that burn relatively cleanly. Bacterial breakdown of plant material produces methane (chapter 10). Under proper conditions, this process can be controlled to produce a clean-burning fuel similar to natural gas. It should be noted, however, that any of these conversions must result in the loss of a portion of the useful energy. The laws of thermodynamics tell us that we would get the most energy by burning the biomass directly rather than converting it to a more convenient liquid or gaseous fuel.

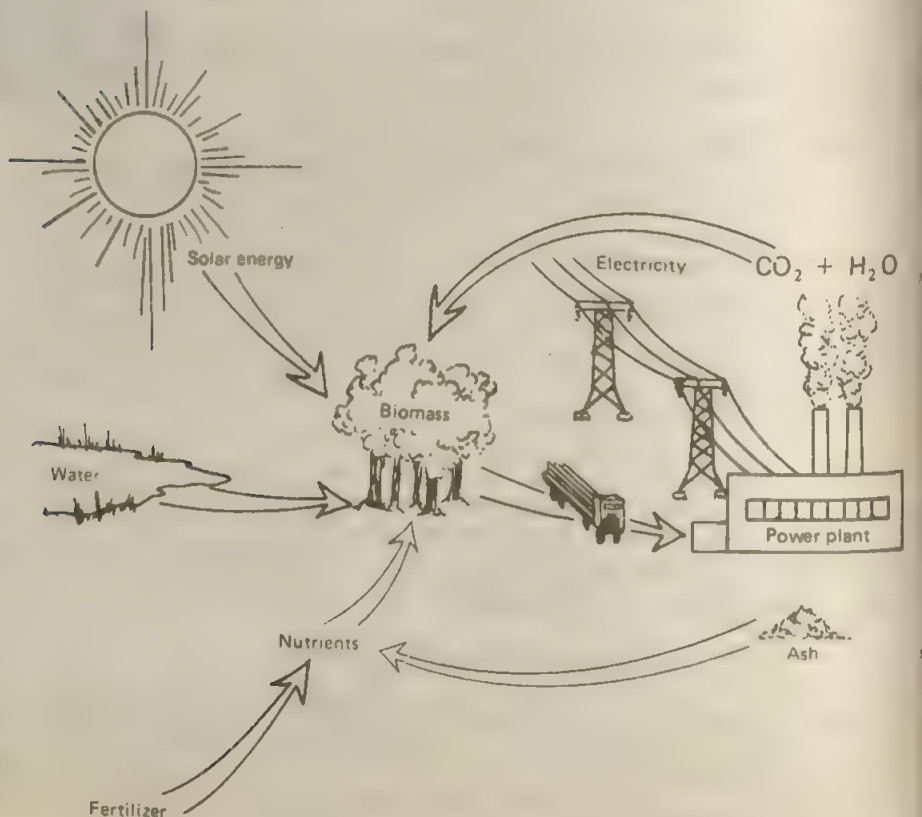


Figure 13.6 Energy from the sun can be converted to electrical energy by way of the green plants. If the ash from the burned plants were not returned to the soil, the soil would become depleted in nutrients and would have to be fertilized. Indeed, most of the land being considered for biomass production is too poor to be productive without massive applications of fertilizer.

The shortage of land probably means that we would never obtain a major portion of our energy from biomass. We could, however, supplement our other sources by burning agricultural wastes, fermenting some to ethyl alcohol, producing methyl alcohol from wood where wood is plentiful, and fermenting human and animal wastes to produce methane. The technology for all these processes is readily available. Each has been used in the past. Several of the processes now are being used on a limited scale or are being investigated for use in the future. For example, a wood-burning power plant is now being built in Maine.

We also could obtain energy by burning the combustible portion of garbage. This material—mostly paper—could be separated and burned as a supplement to coal for generating electricity. The noncombustible portion of garbage is mostly glass and metal. These can be readily recycled (chapter 9).

Wind and Water: Once and Future Energy Sources

The sun, by heating the Earth, causes the winds to blow and the water to evaporate and rise in the air, later to fall as rain. The blowing wind and the flowing water can be used as sources of energy. Indeed, they have been used that way for centuries. Waterwheels were used to lift water into the irrigation ditches of ancient Egypt. Windmills were used in tenth-century Persia to grind grain.

Why not use windpower and waterpower to solve the energy crisis? We do use waterpower. About 4% of our current energy production is hydroelectric, most of it in the mountainous western United States. In the modern hydroelectric plant, water is held behind huge dams. Some of this stored water is released against the blades of water turbines. The potential energy of the stored water is converted to the kinetic energy of flowing water. The moving water imparts mechanical energy to the turbine. The turbine drives a generator that converts mechanical energy into electrical energy.

Hydroelectric plants are relatively clean, but most of the best dam sites in the United States have already been used. To obtain more hydroelectric energy, we would have to dam up scenic rivers and flood valuable cropland and recreational areas. Reservoirs silt up over the years, and sometimes dams break, causing catastrophic floods. Even hydroelectric power has its problems.

We could use more windpower. The kinetic energy of moving air is readily converted to mechanical energy to pump water and grind grain. Windmills have been so used for centuries.

Wind also can be used to turn turbines and generate electricity. Giant windmills have been built to test and develop this potential (figure 13.8). Smaller units are available for use on farms and rural dwellings (figure 13.9). It may be that these smaller units will have greater potential than the huge ones when more people move into self-sufficient dwellings.

Properly developed, windpower could easily supply 10% of our energy needs. Wind is clean, free, and abundant. However, one serious drawback is that the wind does not always blow. Some means of energy storage or an alternate source of energy must be available. Land use might become a problem if windpower were used widely. Presumably, land under windmills could be used for farming or grazing, but giant complexes with powerlines would be ugly. Perhaps most serious of all, though, is the fact that the wind turbines interfere with television reception.

Moon Power: The Tides

The power of the tides is another potential source of energy. One tide-powered generating plant is now in operation in France. Although the tides produce great amounts of energy, there are few appropriate sites available in the United States.

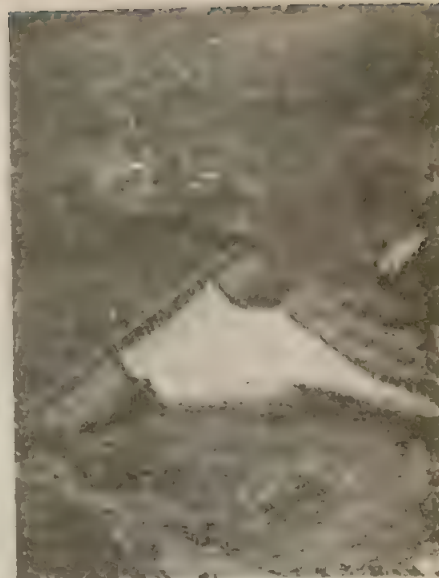


Figure 13.7 The Grand Coulee Dam on the Columbia River in Washington State produces over 5000 Mw of electrical energy. (Courtesy of the Bureau of Reclamation, United States Department of the Interior. Photo by H. S. Holmes.)



Figure 13.8 An experimental 200-kw wind turbine generator is being tested in Clayton, N.M. (Courtesy of the United States Department of Energy, Washington, D.C.)



Figure 13.9 This wind-driven power unit once furnished 110 v of electricity to a cafe/general store and several buildings surrounding it in Duxbury, Iowa. (Courtesy of the *St. Paul Sunday Pioneer Press*, St. Paul.)



Figure 13.10 The tide comes in on a rocky coast. Are we willing to give up the view for a tide-powered electricity-generating plant? (Courtesy of the Union Pacific Railroad.)

Earth Power: Geothermal Energy

The interior of the Earth is heated by immense gravitational forces and by natural radioactivity. This heat comes to the surface in some areas through geysers and volcanoes. Geothermal energy has long been used in Iceland, New Zealand, and Italy. It has some potential in the United States (indeed, it is being used now in California, **figure 13.11**), but in the near future this potential could only be realized in areas where steam or hot water is at or near the surface. One drawback of geothermal energy is that the wastewater is quite salty. Its disposal could be a major problem.

Oil Shale and Tar Sands: High-Entropy Oil

There are fossil carbon compounds other than coal, petroleum, and natural gas. For example, there are immense reserves of oil shale in Colorado, Utah, and Wyoming, and of tar sands in Alberta, Canada. The problem with both resources is that their extraction is difficult, and environmental disruption is severe.



(a)

Actually, oil shale contains no oil. The organic matter is present as a complex material called *kerogen*, which has an approximate composition of $(C_nH_{2n}O)_n$, where n is a large number. When heated in the absence of air, kerogen breaks down, forming hydrocarbon oils similar to petroleum. The problem is that most of the kerogen is thinly distributed through rock. Although it does not seem to be covalently bonded to the rock, it can't be pumped out as petroleum is pumped from the porous rock in which it occurs. It takes a lot of energy to get oil from oil shale, and there is a lot of waste rock left to dispose of. The energy content of the shale oil, by the time it is refined into gasoline and fuel oil, is not a whole lot greater than the energy put in to producing it.

Tar sands are quite different from oil shale, but the problems associated with extracting the fuel from them are similar. The organic matter of tar sands is present as *bitumen*, a hydrocarbon mixture. Separating bitumen from sand is difficult and requires a lot of energy. Like oil shale, the organic matter is a thin mixture in a lot of inorganic waste.

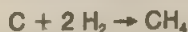
It may be that we will someday get a significant portion of our energy from oil shale and tar sands. It will be expensive energy, though. The thinly distributed, intimately mixed organic matter is high-entropy stuff. To get it into a useful, low-entropy (purified) form will require a lot of energy. The return on the energy invested will most likely be rather low.

Coal Gasification and Liquefaction: Convenience and Waste

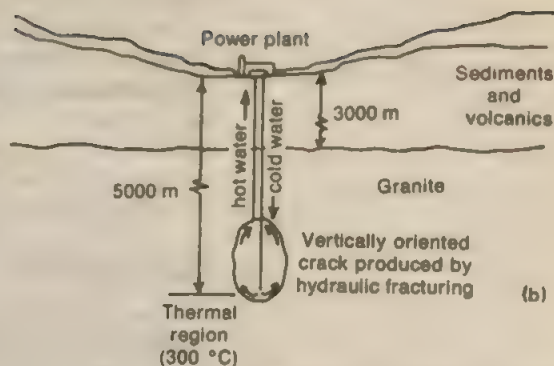
Quite often, in discussions of future energy supplies, we hear about converting coal to gas or oil. We are running short of gas and petroleum. Why not make them out of coal? The technology has been around for years. Why not get on with it?

Gasification and liquefaction have some nice advantages. Gases and liquids are easy to transport (chapter 12). The process of conversion leaves the sulfur behind, thus overcoming one of the serious disadvantages of coal as a fuel.

There are a variety of experimental projects under way in which coal is being converted to a synthetic gaseous fuel. The basic process is one of reduction of carbon by hydrogen.



The hydrogen can be produced by passing steam over hot charcoal.



(b)

Figure 13.11 Geothermal energy has the potential of contributing to our energy supply. (a) A commercial geothermal plant at the Geysers in Sanoma County, California. (b) A scheme for extracting energy from dry, hot rock 5 km below the surface of the Earth. (Photo courtesy of the United States Department of the Interior, Washington, D.C.)

Coal also can be reacted with hydrogen to form petroleum-like liquids from which gasoline and fuel oil can be made.

But both gasification and liquefaction of coal require a lot of energy. The processes are inherently wasteful; up to 33% of the energy content of the coal is lost in the conversion. These processes require large amounts of water, and yet the large coal deposits on which they would be based are in arid regions. Further, the conversions are messy. The plants, without stringent safeguards, would seriously pollute both air and water. To increase our supply of more convenient fossil fuels—oil and gas—we would deplete our third fossil fuel—coal—even more rapidly.

Energy: What For?

The United States, with only 6% of the world's population, uses 33% of all the energy presently being generated. What for? Abundant fuel has enabled the United States to build its industrial base and provide its people with one of the highest standards of living in the world.

Industry uses about 33% of all the energy produced in the United States. This energy is used to convert raw materials into the myriad of products that our society demands. Utilities use about 25% of the nation's energy production, primarily for the generation of electricity. Transportation uses another 25%, mainly to power private automobiles. Private homes use about 14% of the nation's energy.

Energy lights our homes, heats and cools our living and working spaces, and makes us the most mobile society in the history of the human race. It powers the factories that provide us with abundant material goods. Indeed, energy is the basis of our modern society. By the 1970s, many Americans had begun to wonder whether we had sufficient energy resources to sustain this life-style in the years ahead.

Energy: How Much Is Too Much?

Although there are many problems involved, science and technology probably will be able to provide us with a plentiful supply of energy for the foreseeable future. This energy will not—indeed, it cannot—be pollution free. Any production and use of energy will be accompanied by pollution.

How do we choose the best method of energy production? It certainly is a difficult task. The choice should be made by informed citizens who have examined the process from beginning to end. We must know what is involved in the construction of the power plants, the production of the fuels, and the ultimate use of the energy in our homes or factories. We must know that energy is wasted (as heat) at every step in the process. Plentiful power involves severe thermal pollution in the areas where power is generated, for we cannot escape the long arm of the second law.

Will our profligate consumption of energy affect the Earth's climate? Our activities have already modified the climate in and around major metropolitan areas. If present trends continue, it is estimated (reference 5, chapter 12) that waste heat released in the Boston-to-Washington metropolitan area will be equivalent to 30% to 50% of the solar radiation at ground level. This cannot fail to affect seriously the climate in that area. The worldwide effects of our expanding energy consumption are harder to estimate, but, if present trends in population growth and energy consumption continue, we may well reach the limits of our capacity to generate electricity by the year 2150.

What can we do as individuals? We can conserve. We can walk more and use cars less. We can reduce our wasteful use of electricity. We can buy more-efficient appliances, and we can avoid purchasing energy-intensive products. Indeed, several European nations have higher standards of living than the United States and yet use

ess energy per capita. Let's learn from them so that we can save energy and better our lives at the same time.

Problems

1. Your children will not have abundant natural gas and petroleum during the next century. What energy source would you choose for them? Why?
2. Which of the following is the best fuel for heating your home?
 - a. natural gas
 - b. electricity
 - c. coal
 - d. fuel oilWhat problems with supply, use, and waste products are involved with each fuel?
3. Where does the electrical energy that you use come from? What pollution problems are associated with its generation?
4. How does a breeder reactor produce more fuel than it consumes?
5. What two fuels can be produced in breeder reactors? Write the nuclear equations by which each is formed.
6. Why can't nuclear bombs be made from reactor-grade uranium?
7. Human and animal wastes can be fermented to produce methane gas. Can you anticipate any problems that are likely to arise from this process?
8. Some cities burn rubbish to produce steam for the generation of electricity. Find out if your local government has considered this source of energy.
9. Your school probably produces a lot of wastepaper. Could this be burned to heat the buildings in winter? What problems might be involved?
10. Compare a nuclear power plant with a coal-burning one. Which would you rather have in your neighborhood? Why?
1. Do you consider thermal pollution a problem for your local area or the Earth as a whole?
2. Who should decide if and when energy should be rationed?
3. Discuss each of the following as a future energy source. List the advantages, the disadvantages, and the limitations of each.
 - a. nuclear fusion
 - b. solar power
 - c. windpower
 - d. geothermal power
 - e. power from the tides
 - f. power from the biomass
 - g. hydroelectric power
 - h. oil shale
 - i. tar sands
4. What are the advantages and the disadvantages of coal gasification and liquefaction?
5. What factors will ultimately limit the production and use of energy on Earth?

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chapter 14

Polymers: Giants among Molecules

For the most part, chemistry is a study of molecules. Most of the molecules that we have discussed so far have been simple ones composed of only a few atoms each. One exception was DNA, the giant molecule that controls heredity (chapter 11). A single molecule of DNA may contain several million atoms. Many other familiar substances, such as the starches and the proteins (chapter 16), also are made up of giant molecules. (You should realize that these molecules are giants only when compared to the usual small molecules; most are still invisibly small.)

Chemists call these molecular giants *macromolecules* (from the Greek *makros*: “large” or “long”). The naturally occurring ones just mentioned are the stuff of which living things are made. Macromolecules also have served humanity for centuries in the form of wood, wool, cotton, and silk, which are used for housing and clothing. In the form of starches and proteins, macromolecules are foodstuffs.

It took scientists many years to discover that at least some of the special properties of these substances, particularly their physical properties such as tensile strength and flexibility, were related to the enormous size of their molecules. And it took them even longer to determine the structure of giant molecules. The major finding of the experiments was that the giant molecules are constructed from “building blocks”—smaller, repetitive units, like the bricks that make up a wall.

The temptation to improve on nature has always been great, and it has rarely been resisted. Chemists studying natural macromolecules soon learned to produce their own, which they designed to fit specific purposes and to enhance certain properties that suited those purposes. Quite often, chemists were able to improve on nature’s handiwork.

Polymers: Making Big Ones Out of Little Ones

These macromolecular materials have come to be known to the general public as *plastics*. Not all substances made of giant molecules are plastic, however, at least not in the scientific sense. In scientific terminology, the word *plastic* describes a substance that can be softened by heat and formed by pressure. To the nonchemist,

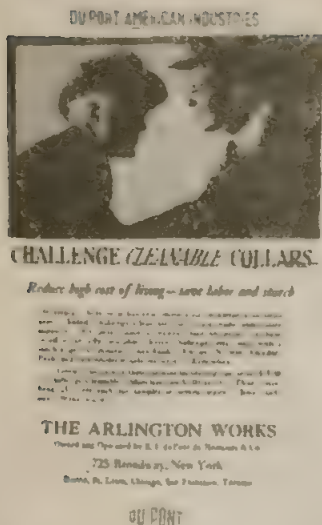


Figure 14.1 Celluloid, a nitrocellulose product, was the first synthetic plastic. Around the turn of the century, many commercial uses were found for celluloid. (Courtesy of E. I. du Pont de Nemours and Company, Inc., Wilmington, Del.)

however, the process of manufacture is not readily apparent and the word *plastic* means any of a variety of structural materials, films, and fibers.

Chemists call a macromolecular substance a *polymer* (from the Greek *poly*: "many," and *meros*: "parts"). Polymers usually are made in the laboratory by the combination of many small molecules into much larger molecules with significantly different properties. The small molecules—the building blocks—are called *monomers* (from the Greek *monos*: "one"). A polymer is as different from a monomer as long spaghetti noodles are from the powdery wheat flour that spaghetti is made of. For example, polyethylene, the familiar solid, waxy "plastic" in plastic bags, is a polymer prepared from a monomer (ethylene) which is a gas.

Improving on Nature: Billiard Balls and Celluloid Collars

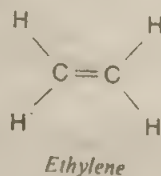
The oldest attempts to improve on nature simply involved chemical modification of the natural macromolecules. The synthetic material celluloid, as its name implies, was derived from natural cellulose. When cellulose is treated with nitric acid, a derivative called cellulose nitrate is formed. In response to a contest to find a substitute for ivory for use in billiard balls, John Wesley Hyatt, an American inventor, found a way to soften cellulose nitrate by treating it with ethyl alcohol and camphor. The softened material could be molded into smooth, hard balls. How many of us could afford to have a pool table in our basements if we had to buy ivory billiard balls? Hyatt brought the game of billiards into the economic reach of working people.

Celluloid also was used in movie film and stiff collars, which didn't require repeated starching (figure 14.1). Because of its dangerous flammability (cellulose nitrate also is used as smokeless gunpowder), celluloid was removed from the market when safer substitutes became available. Today, movie film is made from cellulose acetate, another semisynthetic modification of cellulose. And high, stiff collars on men's shirts are out of fashion.

It didn't take long for the chemical industry to recognize the potential of synthetics. Scientists both in and out of industry began making macromolecules from scratch, starting with small molecules rather than modifying large ones. The first such truly synthetic polymers were the phenol-formaldehyde resins, first made in 1910. These complex polymers are discussed later in this chapter. Let's look at some simpler ones first.

Polyethylene: From the Battle of Britain to Bread Bags

Polyethylene is the simplest of the synthetic polymers, and it's the cheapest, too. It is familiar today as the plastic bags used for packaging fruit and vegetables, garment bags for dry-cleaned clothing, garbage can liners, and many other items. Polyethylene is made from ethylene. This unsaturated hydrocarbon (chapter 10) is produced in large quantities from the cracking of petroleum.



Ethylene molecules, under high pressure and temperature and in the presence of a catalyst, are made to join together in long chains. The polymerization can be represented by the reaction of a few monomer units.

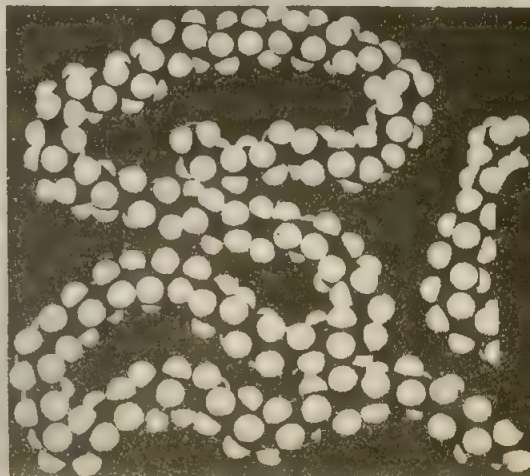
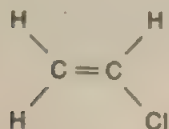




Figure 14.4 These three bottles are made of polyethylene and were heated in the same oven for the same length of time. Those that melted have branched polyethylene molecules; the other is composed of unbranched chains. (Photo by Mari Ansari.)



Vinyl chloride



Figure 14.5 Some vinyl objects. (Photo by Dennis Tasa.)

Figure 14.6 Framework model of a segment of a polyvinyl chloride molecule. (Courtesy of Science Research Materials, Inc., Janesville, Wis.)

refrigerator dishes, insulation for electrical wiring, squeeze bottles, and many other common household articles.

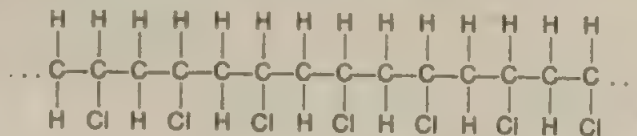
Polyethylene is a *thermoplastic* material, that is, it can be softened by heat and then reformed. (Another class of polymers, called *thermosetting* polymers, are permanently hardened when formed; we look at some of that type shortly.) Polyethylene is the most important plastic on the market today. Production in the United States reached 5.14 billion kg in 1978. That was 23 kg for each of the 220 million people in the United States, and the per capita use is still increasing!

The Vinyl Solution

Would you like a tough synthetic material that looks like leather and yet costs only a fraction as much? Would you like a clear, rigid material from which unbreakable bottles could be made? Would you like an attractive, long-lasting floor covering? How about inexpensive phonograph records that give excellent sound reproduction? The solution to each of your desires would be a vinyl one. A synthetic material called polyvinyl chloride (PVC) has all these properties—and more.

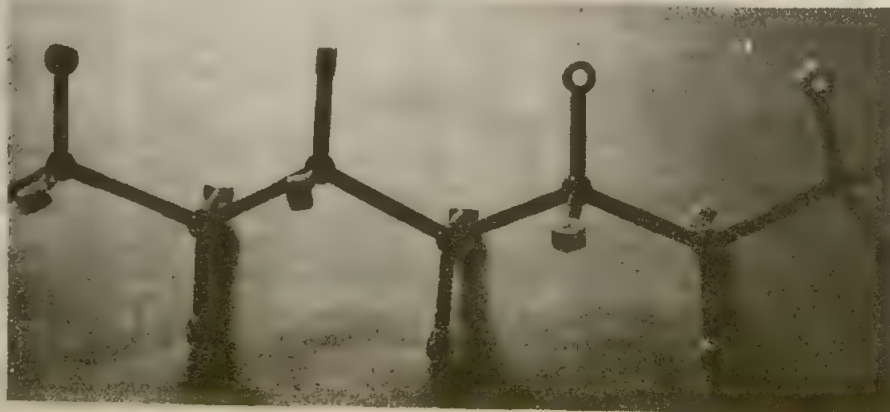
The properties of a polymer, like those of other substances, can be changed by varying its molecular architecture. Replacing one of the hydrogen atoms of ethylene with a chlorine atom gives a compound called vinyl chloride. This compound is a gas at room temperature. It is insoluble in water. For polymerization, it is suspended, under pressure, as tiny droplets in water. The heat that is generated by the reaction is readily dissipated by the water.

A two-dimensional representation of the structure of a segment of a polyvinyl chloride molecule is illustrated below. The structure of polyvinyl chloride differs from that of ethylene by having a chlorine atom on every other carbon atom. A three-dimensional, framework model is illustrated in figure 14.6.



Polyvinyl chloride

PVC is readily formed in a variety of shapes. The clear, transparent polymer is used in plastic wrap and in clear plastic bottles. To simulate leather—or simply to make the material more attractive—coloring is added and the surface is textured. In



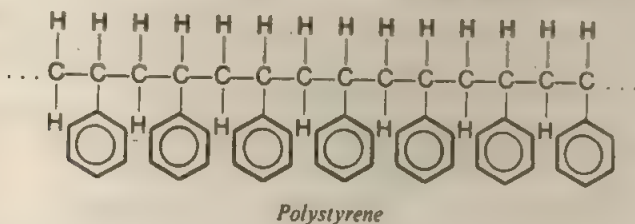
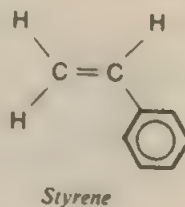
1978, United States industries produced about 2.73 billion kg of vinyl plastics. Not only has this synthetic material gone a long way toward replacing scarce and expensive natural materials, but it has proven to be superior to natural materials for many applications.

Vinyl chloride, the monomer from which vinyl plastics are made, is known to be a *carcinogen*; it causes cancer in some of the people who work where it is made or used. We discuss cancer-causing chemicals in some detail in chapter 24.

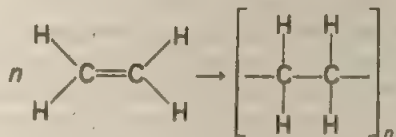
Addition Polymerization: One + One + One . . . Gives One!

There are two general types of polymerization reactions; one is called *addition polymerization* and the other is known as *condensation polymerization*. In addition polymerization, the building blocks (or monomers) add to one another in such a way that the polymeric product contains all the atoms of the starting monomers. The polymerization of ethylene to form polyethylene and of vinyl chloride to form polyvinyl chloride are examples. Notice that in the structure of polyethylene (p. 179), the two carbons and the four hydrogens of each monomer molecule are incorporated into the polymer structure. (In condensation polymerization, a portion of the monomer molecule is *not* incorporated in the final polymer but is split out as the polymer is formed. This process is discussed later in this chapter.)

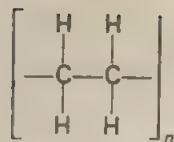
There are many familiar addition polymers. Most are made from monomers that can be considered to be derivatives of ethylene in which one or more of the hydrogen atoms are replaced by another atom or group. For example, we saw in the preceding section that vinyl chloride is derived from ethylene by replacing one of the hydrogen atoms with a chlorine atom. Similarly, replacing one of the hydrogen atoms with a benzene ring gives a monomer called styrene. Polymerization of styrene produces polystyrene, the plastic from which *Styrofoam* insulation and other materials are made. A segment of a polystyrene molecule is illustrated below.



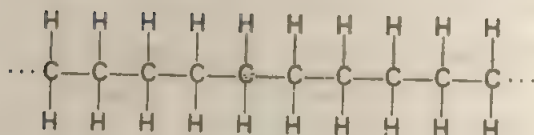
The polymer structures and polymerization equations we have written are quite cumbersome. There are other ways of writing the formulas for polymers and the equations for polymerization reactions, ways that do not involve our writing out long segments of the polymer chain. We can represent the polymerization of ethylene by the equation:



In the formula for the polymer product, the repeating polymer unit (sometimes called the *segmer*, meaning "repeating segment") is placed within brackets with bonds extending to both sides. The subscript *n* indicates that this molecular fragment is repeated an unspecified number of times in the full polymer structure. It is certainly easier to write



than



but the second formula is probably better at conveying the concept of a polymer as a giant molecule (even though this formula also represents only a small portion of the whole molecule).

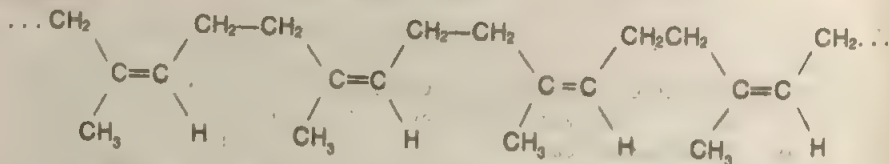
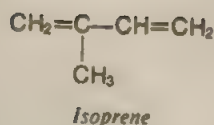
The simplicity of the abbreviated formula does facilitate certain comparisons between the monomer and the polymer. Notice that the monomer ethylene contains a double bond while polyethylene does not. The double bond of the reactant contains two pairs of electrons. One of these pairs is used to connect one monomer unit to the next in the polymer (indicated by the lines sticking out to the sides in the segment). That leaves only a single pair of electrons between the two carbons of the polymer segment; in other words, a single bond. Note that each segment unit in the polymer has the same composition (C_2H_4) as the monomer.

We could not attempt to discuss all the important addition polymers here. Table 14.1 describes a few of the more interesting ones and some of their uses.

Out of War: The Plastics Industry

The plastics industry really got going during and after World War II. After the war cut off the Allies' supply of natural rubber, the plastics industry developed, to a large extent, out of the search for synthetic substitutes for rubber.

Natural rubber can be broken down into a simple hydrocarbon called isoprene. The macromolecules from which rubber is made are now known to have the structure:



Isoprene is a volatile liquid. Rubber is a semisolid, elastic material.

The long-chain molecules that make up rubber can be coiled and twisted and intertwined with one another. The stretching of rubber corresponds to the straightening of the coiled molecules. Natural rubber is soft and tacky when hot. It can be made harder by reaction with sulfur. This process, called *vulcanization*, cross-links the hydrocarbon chains with sulfur atoms (figure 14.7). Its three-dimensional cross-linked structure makes vulcanized rubber a harder, stronger substance that is suitable for automobile tires. Surprisingly, cross-linking also improves the elasticity of rubber. With just the right degrees of cross-linking, the individual chains are still relatively free to uncoil and stretch. And, when a stretched piece of this material is released, the cross-links pull the chains back to their original arrangement (figure 14.8). Rubber bands owe their snap to this sort of molecular structure.

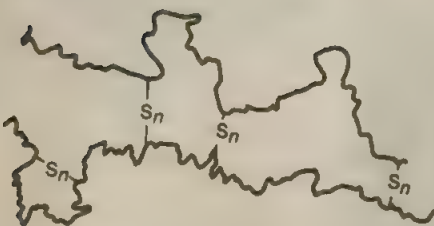


Figure 14.7 Vulcanized rubber. The subscript n indicates an indefinite number, usually between 1 and 4.

Table 14.1
A selection of addition polymers

<i>Monomer</i>	<i>Polymer</i>	<i>Polymer Name</i>	<i>Some Uses</i>
$\text{H}_2\text{C}=\text{CH}_2$	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{H} \end{array} \right]_n$	Polyethylene	Plastic bags, bottles, toys, electrical insulation
$\text{H}_2\text{C}=\text{CH}-\text{CH}_3$	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{CH}_3 \end{array} \right]_n$	Polypropylene	Indoor-outdoor carpeting, bottles
$\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{H}_5$	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{C}_6\text{H}_5 \end{array} \right]_n$	Polystyrene	Simulated wood furniture, styrofoam insulation and packing materials
$\text{H}_2\text{C}=\text{CH}-\text{Cl}$	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{Cl} \end{array} \right]_n$	Polyvinyl chloride, PVC	Plastic wrap, simulated leather (Naugahyde), phonograph records, garden hoses
$\text{H}_2\text{C}=\text{CCl}_2$	$\left[\begin{array}{cc} \text{H} & \text{Cl} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{Cl} \end{array} \right]_n$	Polyvinylidene chloride, <i>Saran</i>	Food wrap
$\text{F}_2\text{C}=\text{CF}_2$	$\left[\begin{array}{cc} \text{F} & \text{F} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{F} & \text{F} \end{array} \right]_n$	Polytetrafluoroethylene, <i>Teflon</i>	Nonstick coating for cooking utensils, electrical insulation
$\text{H}_2\text{C}=\text{CH}-\text{CN}$	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{CN} \end{array} \right]_n$	Polyacrylonitrile, <i>Orlon</i> , <i>Acrilan</i> , <i>Creslan</i> , <i>Dynel</i>	Yarns, wigs
$\text{H}_2\text{C}=\text{CH}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3 \end{array} \right]_n$	Polyvinyl acetate, PVA	Adhesives, textile coatings, chewing gum resin, paints
$\text{H}_2\text{C}=\overset{\text{CH}_3}{\underset{\text{O}}{\parallel}{\text{C}}}-\text{O}-\text{CH}_3$	$\left[\begin{array}{cc} \text{H} & \text{CH}_3 \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{C}-\text{O}-\text{CH}_3 \\ \parallel \\ \text{O} \end{array} \right]_n$	Polymethylmethacrylate, <i>Lucite</i> , <i>Plexiglass</i>	Glass substitute, bowling balls

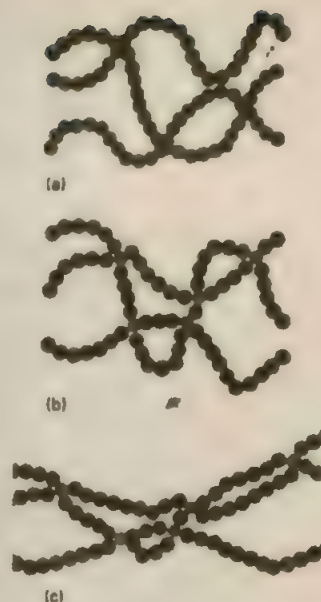


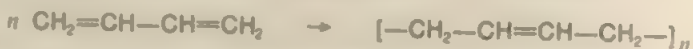
Figure 14.8 Vulcanization of rubber cross-links the molecular chains. (a) In unvulcanized rubber, the chains slip past one another when the rubber is stretched. (b) Vulcanization involves the addition of sulfur cross-linkages between the chains. (c) When the vulcanized rubber is stretched, the sulfur cross-linkages prevent the chains from slipping past one another. Vulcanized rubber is stronger and more elastic than unvulcanized rubber.



Butadiene

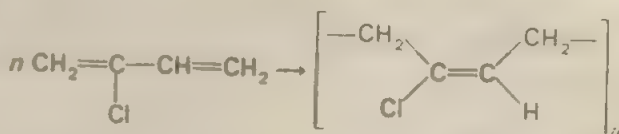
Synthetic Elastomers: More Bounce to the Ounce

Synthetic polymers with rubberlike properties are called *elastomers*. Natural rubber is polymer of isoprene. Some synthetic elastomers are closely related to it. For example, polybutadiene is made from the monomer butadiene. Butadiene differs from isoprene only in that it lacks a methyl group on the second carbon atom. Polybutadiene is made rather easily from the monomer:

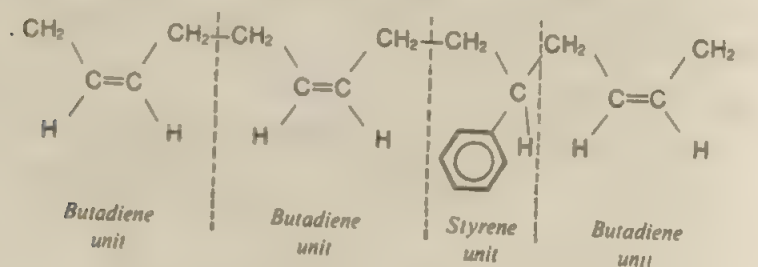


However, it has only fair tensile strength and poor resistance to gasoline and oils. These properties make it of limited value for automobile tires; the main use of elastomers.

Another synthetic elastomer, polychloroprene (*Neoprene*) is made from a monomer that is quite similar to isoprene but that has a chlorine in place of isoprene's methyl group.



Another of the synthetic rubbers illustrates the principles of *copolymerization*. In this process, a mixture of two monomers forms a product in which the chain contains units of both building blocks. Such a material is called a *copolymer*. SBR rubber is a copolymer of styrene (25%) and butadiene (75%). A segment of an SBR molecule might look something like this:



This synthetic is more resistant to oxidation and abrasion than natural rubber but has less satisfactory mechanical properties.

Like natural rubber, the SBR molecules contain double bonds and can be cross-linked by vulcanization. SBR rubber accounts for over 50% of the total production of elastomers. Production in the United States in 1978 was 1.40 billion kg of SBR out of a total elastomer production of 2.48 billion kg.

Chemists even have learned to make polyisoprene, a substance identical in every way to natural rubber except that it comes from petroleum refineries rather than plantations of rubber trees.

In addition to elastomers (mainly SBR), tires for automobiles contain many other substances. Carbon black is added before vulcanization. It acts in some as yet unknown way to strengthen the elastomer. The tire is further strengthened mechanically by the use of rayon or nylon cord, by the use of fiberglass, and even by the use of steel belts.

Painting with Polymers

The development of the plastics industry following World War II has revolutionized many aspects of modern society. Not the least affected has been the paint industry. Even the process of painting has been dramatically changed by the development of water-based paints.

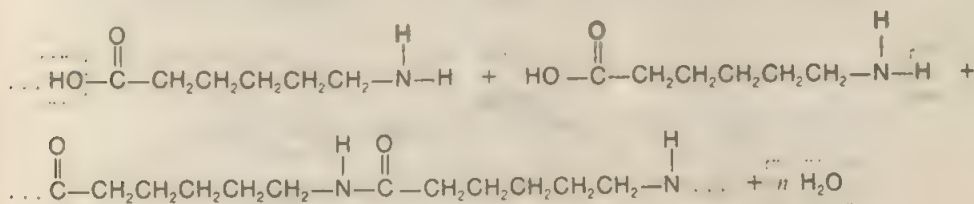
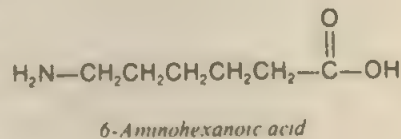
A paint usually is composed of three components: (1) a binder (or vehicle) that hardens to form a continuous film; (2) a pigment that supplies the desired color; and (3) a volatile solvent that evaporates.

In oil-based paints, linseed oil often is used as a binder. The solvent is usually turpentine, a mixture of hydrocarbons obtained from pine trees. The pigment can be titanium dioxide (TiO_2 , white), carbon black (C), chrome yellow (PbCrO_4), oxides of iron (brown or red), or organic dyes of various colors. White lead [with an approximate composition of $\text{Pb}(\text{OH})_2 \cdot 2 \text{PbCO}_3$] was once used extensively, but it has been banned for interior use because of the high toxicity of lead. Illnesses in infants and toddlers, particularly in ghetto areas, have been attributed to the ingestion of chips of old, peeling lead paint.

In water-based paints, a synthetic polymer with rubberlike properties is used as the binder. These latex paints are emulsified in water to give a variety of spreading characteristics. Dyes and pigments can be added to produce the desired colors. Among the plastics used in latex paints are polyvinyl acetate, polymethyl methacrylate (or related acrylic latexes), polystyrene, styrenebutadiene copolymers, and polytetrafluoroethylene (*Teflon*). Paints can be formulated to have a fantastic variety of colors, textures, and resistancies.

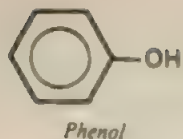
Condensation Polymers: Splitting Out Little Ones to Make Big Ones

The polymers considered so far are all addition polymers. All the atoms of the monomer molecules are incorporated into the polymer molecules. In condensation polymerization, a portion of the monomer molecule is not incorporated in the final polymer. As an example, let's consider the formation of one type of nylon. (There are several different nylons, each prepared from a different monomer or set of monomers, but all share certain common structural features. We discuss another kind of nylon later in this chapter.) The monomer in this type of nylon is a carboxylic acid with an amino group on the sixth carbon atom, 6-aminohexanoic acid. The polymerization involves the reaction of a carboxyl group of one monomer molecule with the amine group of another. This reaction produces an amide bond that holds the building blocks together in the final polymer.



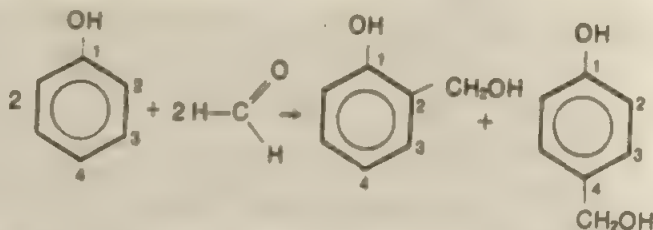
Water molecules are formed as a by-product. It is this formation of a nonpolymeric by-product that distinguishes condensation polymerization from addition polymerization. Note that the formula of the segment unit is *not* the same as that of the monomer.

As our next example, let's consider *Bakelite*. These phenol-formaldehyde resins were first synthesized in 1910. They are made, as the name indicates, from

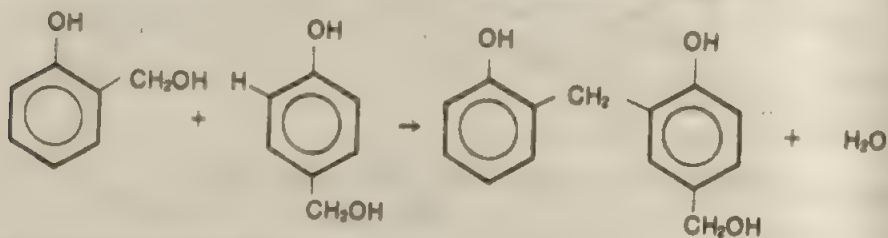


formaldehyde, the simplest of the aldehydes (chapter 11), and phenol, an aromatic compound related to benzene (chapter 10) and the alcohols.

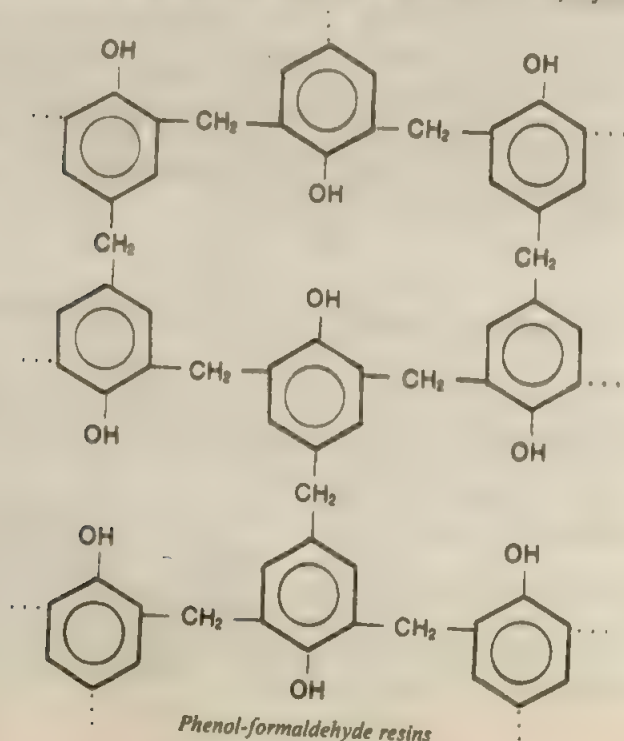
The phenol-formaldehyde resins are formed by splitting out water molecules, the hydrogen atoms coming from the benzene ring and the oxygen atoms from the aldehyde. The reaction proceeds stepwise, with formaldehyde adding first to the 2- and 4- positions of the phenol molecule.



The substituted molecules then interact by splitting out water (remember that there are hydrogen atoms at all the unsubstituted corners of a benzene ring).



The hookup of molecules continues until an extensive network is achieved. Water is driven off by heat as the polymer sets. The structure of the polymer is extremely



complex. It exists as a huge, three-dimensional network somewhat like the framework of a giant building. A schematic representation of part of such a molecule is illustrated on p. 186. Note that the phenolic rings are joined together by CH₂ units from the formaldehyde.

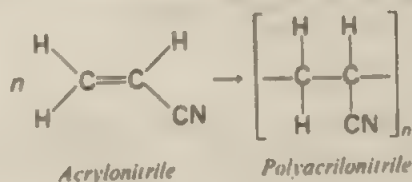
Recall that polyethylene is thermoplastic; it can be softened by heat and then reformed. Phenol-formaldehyde resins are representative of a group called *thermosetting* plastics. These are fusible at some stage of their production but become permanently hard under the influence of heat and pressure. They cannot be softened and remolded.

Thermoplastic polymers can be recycled rather easily. They can be melted down and remolded. Recently, methods have been developed for the recycling of some thermosetting plastics. These methods work by breaking the large molecules down to smaller ones that can be converted into the original monomers. Both types of recycling consume energy, but the biggest problem in recycling plastics is their collection and separation. Not only must the plastics be separated from other types of solid wastes, but the various kinds of polymers must be separated from each other—PVC from polyethylene, and so on.

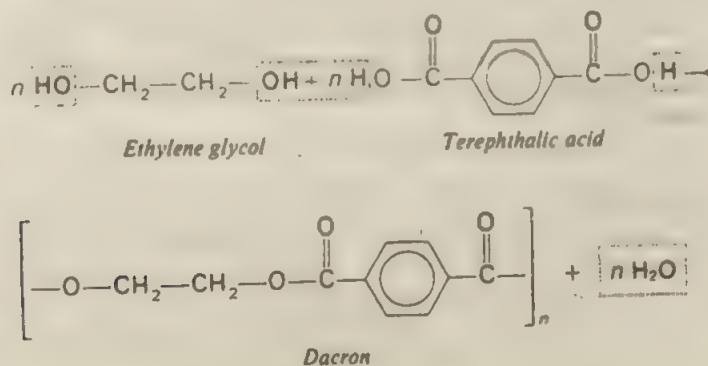
Fibers and Fabrics

Let's consider another area in which synthetics have mimicked nature's work successfully. Cotton, wool, and silk have long been spun and woven into fabrics for clothing and other uses. The fibrous nature and, particularly, the great tensile strength of these materials were perfectly suited to such purposes. In the last few decades, synthetic polymers with similar physical properties have revolutionized the clothing industry and have outdone the natural fibers in their resistance to stretching and shrinking (and to moths).

Both addition and condensation polymerization have yielded useful materials. Polyacrylonitriles (*Orlon*, *Acrlan*, *Creslan*, and the like) are addition polymers.

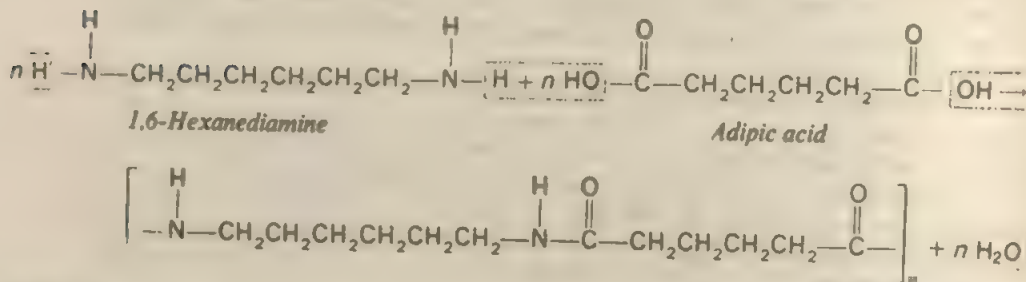


These acrylic fibers are used in clothing, carpets, and so on. Polyesters (*Dacron*) and polyamides (nylon) are condensation polymers. *Dacron* polyester is made through the condensation of ethylene glycol with terephthalic acid.



Polyester fibers are used in wash-and-wear clothing. The same polymer, when formed as a film rather than fiber, is called *Mylar*. When magnetically coated, *Mylar* tape is used in audio and video recording.

The most common polyamide, *Nylon 66**, also is made by the condensation of two different monomers.



Silk and wool, which are natural protein fibers, are also polyamides. All these fibers, like high-density polyethylene, owe their strength to the ordered, relatively rigid arrangement of their long molecules. However, the polyamides and polyesters possess features not shared by polyethylene. The former compounds contain polar functional groups, and the interaction of these groups gives these polymers their unique tensile strength.

*Nylons are named according to the number of carbon atoms in each monomer unit. There are six each in 1,6-hexanediamine and adipic acid; hence, the polymer is *Nylon 66*. The nylon on p. 185 is made from a single monomer that contains six carbon atoms, so it is called *Nylon 6*.

Bulk Properties of Polymers

There are many other types of polymers, both synthetic and natural. The molecules are large, and variations in their structures (and consequent variations in their properties) are almost unlimited. The development of synthetic polymers has led to a whole new world of plastics, rubber substitutes, and synthetic fibers. There is no sharp line separating these types of polymers. The same basic material can be used in two (or even three) of the categories. Nylon, for example, can be molded to make plastic toys or television cabinets, or it can be spun into a fiber and woven into cloth. The major differences between polymer types lie mainly in the organization of the big molecules into bulk materials. The molecules of elastic materials are randomly oriented and tangled with one another. On the other hand, molecules in fibers of high tensile strength are highly organized, even crystalline in arrangement (figure 14.10).

Giant molecules also can impart great structural strength. The great strength of wood, for example, is due in large part to the arrangement of giant cellulose molecules (chapter 16) in a matrix of lignin. The many synthetic substitutes for wood are attempts at duplicating the structural strength of the natural polymer.

The techniques for designing materials have become so far refined that a seemingly impossible combination of properties can be incorporated into a single substance. For example, spandex fibers (which are used for stretch fabrics [*Lycra*] in ski pants, girdles, and bathing suits) combine the elasticity of rubber (necessitating coiled, flaccid molecular chains) and the tensile strength of a fiber (necessitating a

Figure 14.9 A giant bubble of tough, transparent plastic packaging film emerges from the die of an extruding machine. (Courtesy of Reynolds Metals Company)

crystalline arrangement of fairly rigid, highly ordered chains. How can scientists make materials like spandex? By grafting two molecular structures onto one polymer chain. Blocks of components with fibrous character are alternated with blocks of elastomer in the same giant molecule, and the fabric made from the polymer exhibits **both sets of properties, flexibility and rigidity!**

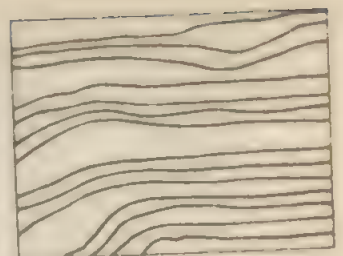
Only a few of the many uses of plastics have been mentioned here. Clothing, containers, kitchenware, synthetic foam rubber for furniture padding, skis, ski boots, bottles and bottle caps, artificial arteries and bone joints, radio and stereo cabinets, windows, windshields, outdoor signs, and protective coatings are only a start of any list of the plastic items that have added so much to our way of life. Plastics play a vital part in our recreation, communication, and personal well-being and in the decoration of our homes, offices, and commercial buildings. Plastics have become very much a part of our lives—and a part of our problems.

Plasticizers and Pollution

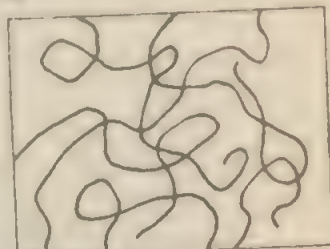
It is difficult to process some plastics, particularly the vinyl types. As formed, they can be rather hard and brittle. But they can be made more flexible and easier to handle by addition of chemicals called *plasticizers*. Ideally, these substances are liquids of low volatility. They serve as internal lubricants. Undiluted polyvinyl chloride (PVC) cracks and breaks easily, but with proper plasticizers added, it is soft and pliable. Plastic raincoats, garden hoses, and seat covers for automobiles can be **made from the modified PVC**.

Plasticizers are generally lost by diffusion and evaporation as a plastic article ages. The plastic becomes brittle and then cracks and breaks. The plasticizers in seat covers sometimes show up on car windows as a "fog" that is almost impossible to remove.

One type of plasticizer once used widely but now largely banned is the polychlorinated biphenyls (PCBs). These compounds are derived from a hydrocarbon—biphenyl ($C_{12}H_{10}$)—by the replacement of anywhere from 1 to 10 of the hydrogen atoms with chlorine atoms. The structures of the parent compound and some of the PCBs are shown in **figure 14.11**. Note the structural similarity of the PCBs to DDT. PCB residues have been found in fish, birds, water, and sediments. The physiological effect of PCBs is similar to that of DDT, with long-term effects of greater concern than acute toxicity. Poultry and eggs have been found to have concentrations greater than the 5 ppm allowed by the Food and Drug Adminis-



(a)



(b)

Figure 14.10 Organization of polymer molecules. (a) Crystalline arrangement. (b) Amorphous arrangement.

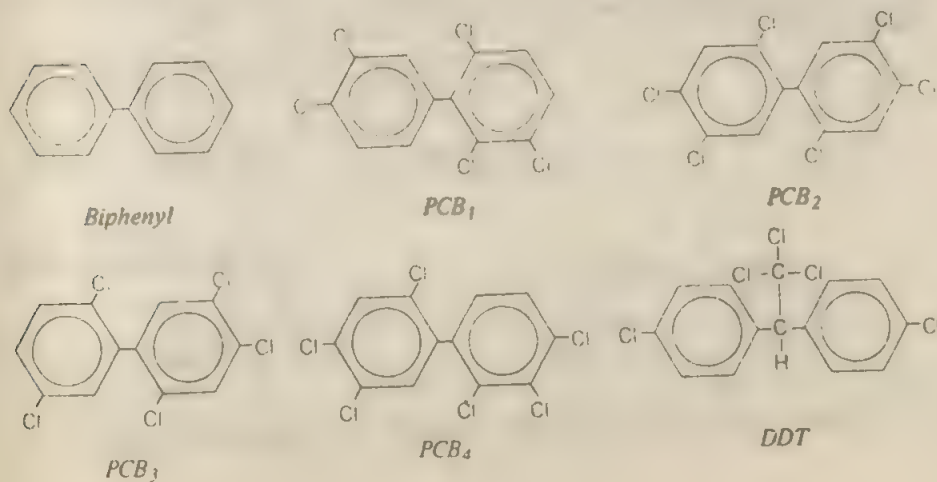


Figure 14.11 Biphenyl and some of the PCBs derived from it. Note that PCB₁ and PCB₂ are isomers with the formula $C_{12}H_8Cl_2$. These are but a few of the hundreds of possible PCBs. DDT is shown for comparison.

tration. Under the law, the contaminated poultry products had to be destroyed. Fish taken from major rivers from coast to coast in the United States also have been found to be contaminated with PCBs, at levels that are often above the 5 ppm maximum allowed by the Food and Drug Administration.

Not all the PCBs manufactured were used as plasticizers. They also were used in electrical equipment. PCBs have a high electrical resistance, making them useful as insulating materials in transformers, condensers, and other electrical apparatus. They also have high boiling points, making them useful as heat-transfer media. PCBs have a density greater than that of water and hence they are often added to lubricants intended for underwater use.

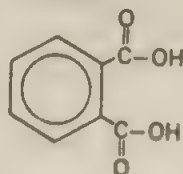
The same properties that made the PCBs so desirable as industrial chemicals—particularly their stability and solubility—cause them to be an environmental hazard. They degrade very slowly in nature, and their solubility in nonpolar media—animal fat as well as vinyl seat covers—leads to their concentration in the food chain. In humans, accidental ingestion has caused skin, liver, and gastrointestinal problems. Experiments with monkeys have shown that levels of less than 5 ppm in food interfere with reproduction.

Monsanto Corporation, the only company in the United States that produced PCBs, discontinued production in 1977, but PCBs will remain in the environment for years.

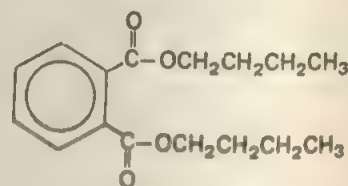
Another class of plasticizers is the phthalates. These compounds are esters derived from phthalic acid. The parent acid and some of the common plasticizers derived from it are shown in figure 14.12. Unlike the PCBs, which are used as a complex mixture, the phthalates are used generally as separate compounds, with individual substances chosen to impart particular levels of flexibility and elasticity to the plastic.

Phthalate plasticizers appear to have low acute toxicity. Their long-term effects are generally unknown. Phthalates have been leached from the PVC bags in which whole blood has been stored. It is thought that these plasticizers may contribute to shock lung, a sometimes fatal condition observed in some patients after a blood transfusion. Phthalates have been found in the heart muscles of cattle, dogs, rabbits, and rats. Very high levels of exposure can induce mutations and birth defects in laboratory animals. What implications, if any, these findings have for human health is not known at this time.

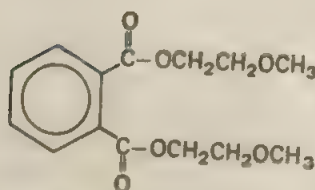
Figure 14.12 Phthalic acid and some derivatives. Dioctyl phthalate is also called di-2-ethylhexyl phthalate (DEHP).



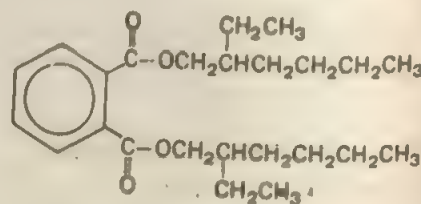
Phthalic acid



Dibutyl phthalate (DBP)



Dimethoxyethyl phthalate (DMEP)



Dioctyl phthalate (DOP)

Plastics and Energy

In chapters 12 and 13, we discussed the ever-increasing demand for energy. One facet of this increase, according to Barry Commoner (reference 5), is the substitution of synthetic materials for natural substances. Production of synthetics involves the use of fossil fuels. Natural materials are renewable, made with energy from the sun. For instance, cotton is produced (by photosynthesis) from carbon dioxide, water, and minerals and with renewable energy from the sun.

The production of nylon, on the other hand, can require as many as 10 steps, each requiring an input of energy (as heat or electric power) that comes ultimately from a nonrenewable source, such as the burning of fossil fuels. Multiply this effect by the thousands of such processes, and you have, in part, the makings of an energy crisis. Also, the raw materials for synthetic polymers come from petroleum. Any shortage of petroleum, then, will cause a shortage of both energy and materials for manufacturing plastics.

What to Do with Them When We're Through with Them

Plastics have become an important part of our litter and solid-waste disposal problems. Perhaps we chemists have done our job too well. We have designed materials that last almost forever! Most plastics decompose very slowly. Once dumped into the environment, they tend to remain there indefinitely. On land, they seem to do little harm, except in an aesthetic sense. Plastics do contribute to the unsightly litter along roadways and elsewhere, and they help provide breeding grounds for disease-carrying insects and rodents. In the water, there are indications of other problems: Fish ingest fragments with their food. Small fish have been found dead, their digestive tracts clogged with pellets of plastic foam.

Plastic materials, like other solid wastes, can be disposed of in sanitary landfills. The problem is that the volume of solid wastes is tremendous, and the land available for use as dumps is rapidly decreasing under the pressure of an increasing population. As a result, large cities are seeking disposal areas hundreds of miles away. And the plastics, though buried, do not rot and go away.

As mentioned earlier (p. 187), we could recycle some plastics. However, the energy required for the collection and separation of them is likely to remain a major obstacle. To date, recycling of plastics is limited mainly to in-house use of scraps in industry.

Many cities burn as much of their solid wastes as possible. Most plastics do burn, but this "solution" to the solid-waste problem leads to increased air pollution. Automobile tires burn with sooty, stinky smoke. Polyvinyl chloride produces toxic hydrogen chloride gas when it burns. Incinerators are corroded by acidic gases and clogged by plastics that melt from the heat without burning. Actually, little information is available about products formed when plastics burn. A great deal of research is needed in the disposal of plastics. We need to know more about the products of their combustion. And we need to know how to control such burning to minimize air pollution. These solutions will require more chemistry, not less, and the research involved will cost a good deal of money.

Biodegradable Polymers

Recent research has led to the development of polymers that break down upon exposure to ultraviolet light or soil microorganisms (figure 14.13). Chemists, who have spent so much time designing materials that will last, are now turning their attention to inventing plastics that will break down after a time. Several different formulations have been developed, but much remains to be done before degradable plastics become an important solution to the litter problem.

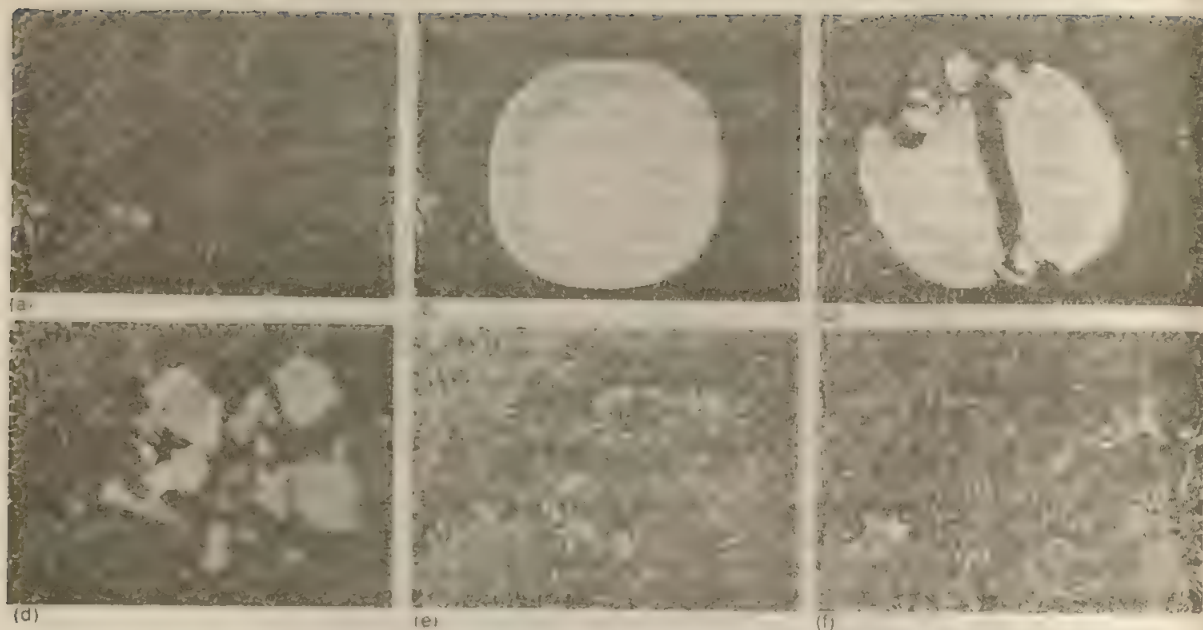


Figure 14.13 This sequence of photos shows the average rate of decomposition of a standard plastic cup lid made with new biodegradable plastic. The decomposition process is a controllable and predictable photochemical reaction. (a) At 0 days, the environment is clean and free of litter. (b) At 5 days, a cup lid made of biodegradable plastic additive is introduced into the environment. (c) After 30 to 90 days, the lid begins to break apart, signaling that decomposition is well under way. (d) After 60 to 120 days, the lid is totally fragmented. (e) After 90 to 150 days, only a fine powder remains. (f) After 6 to 12 months, the environment is once again free of litter. No evidence of the cup lid remains. (Courtesy of Bio-Degradable Plastics, Inc., Sioux Falls, S. Dak.)

Plastics as Fire Hazards

The accidental ignition of fabrics, synthetic or otherwise, has caused untold human misery. The United States Department of Health, Education, and Welfare estimates that as many as 150 000 to 200 000 people are injured and several thousand are burned to death each year in accidents associated with flammable fabrics. While some synthetics are particularly flammable, others may hold the answer to the problem. A good deal of research has been done to develop flame-retardant fabrics. One common approach involves the incorporation of chlorine and bromine atoms within the giant molecules of the polymeric fiber. Federal regulations require that children's sleepwear, in particular, be made of such flame-retardant materials. A major setback to the program occurred in 1977 when the Consumer Product Safety Commission banned a flame-retardant compound called Tris [tris (2,3-dibromopropyl) phosphate], which was used on sleepwear made from polyester and acetate fabrics. In laboratory tests, the compound had been shown to be both carcinogenic and *mutagenic* (mutation inducing). The search for safe fire-retardants continues.

Another problem associated with plastics and fire is that of toxic gases. In December 1972, lethal amounts of cyanide were found in the bodies of plane-crash victims in Chicago. The Illinois Department of Law Enforcement traced the cyanide to burned plastics in the plane's cabin. Firefighters often refuse to enter burning buildings without gas masks for fear of being overcome by fumes from burning plastics. Laboratory tests show that hydrogen cyanide is formed in large quantities by the burning of polyacrylonitrile (*Orlon*, *Creslan*, *Acrilan*, etc.) and other nitrogen-containing plastics. The increasing use of plastics in home furnishings and construction calls for more research in the area of identifying—and quantifying—the products of the combustion of plastics.

Plastics and the Future

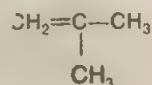
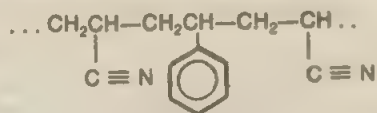
Plastics have provided us with marvelous materials. They also have presented us with problems.

We could do away with plastics. Before you opt for this easy solution, though, look around. What are you ready to give up? The tires, the upholstery, the vinyl hardtop on your car? The keys on your piano? The artificial turf on your athletic field? Your *Styrofoam* cooler? Your telephone? The tile on your floor? Most of your clothes? You would have to give up all these items and many more if plastics were banned.

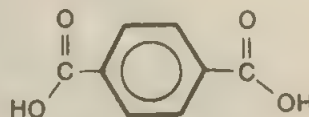
Since the coal and petroleum from which plastics are made are nonrenewable resources, we should use plastics wisely, not wastefully. The thermoplastic materials can be recycled, melted down and remolded. Thermosetting plastics cannot be recycled easily. Perhaps these should be used only in items designed for long-term use and not for disposable gadgets. But plastics, with their problems as well as their promise, are likely to be a part of our lives for a long time to come.

Problems

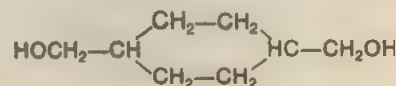
- Define these terms.
 - macromolecule
 - polymer
 - monomer
 - segmer
 - addition polymerization
 - condensation polymerization
 - vulcanization
 - elastomer
 - copolymer
 - plasticizer
- Make a list of plastic objects (or parts of objects) that you encounter in your daily life. Try to identify a few of the kinds of polymers used in making the items. Compare your list with those of some of your classmates.
- How do thermosetting and thermoplastic polymers differ from each other in structure and properties?
- What structural feature usually is found in molecules used as monomers for addition polymerization?
- Why is rubber elastic? How does vulcanization improve its elasticity?
- How do low-density and high-density polyethylenes differ in structure and properties?
- What problems arise when plastics are disposed of in landfills? By incineration?
- Should plastics be totally banned, selectively banned, used without regulation, or used with some regulation? Explain your choice fully.
- Where will plastics come from when the Earth's supplies of coal and petroleum are exhausted?
- Isobutylene polymerizes to form butyl rubber. Write a two-dimensional representation of a segment of the butyl rubber molecule. The segment should contain at least four monomer units. The structure of isobutylene is illustrated in the margin.
- Kodel* is a polyester fiber. The monomers are terephthalic acid and 1,4-cyclohexanedimethanol. Write the structure of a segment of *Kodel* containing at least one of each monomer unit. The structures of the monomers are illustrated in the margin.
- From what monomers might the following copolymer be made?



Isobutylene



Terephthalic acid



1,4-Cyclohexanedimethanol

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chapter 15

Farm Chemistry: Food for a Hungry World

In 1830, Thomas Robert Malthus, an English clergyman and political economist, made the statement that population increases faster than the food supply. Unless the birthrate were controlled, he said, poverty and war would have to serve as restrictions on the increase.

By the late nineteenth century, it appeared that science had thwarted Malthus. Farmers, using fuel, fertilizer, and pesticides, were producing food in fantastic quantities. Indeed, for United States farmers during the 1950s and early 1960s, the major problem was a large surplus of food that led to low prices for their products.

By the late 1960s, however, the ghost of Thomas Malthus had risen to haunt a hungry world. And some scientists began to predict dire consequences from the very same technology that had brought us abundant food. We have already seen (chapter 1) that Rachel Carson predicted that overuse of pesticides would lead to ecological disasters. Let's now look at some other predictions and evaluate them in the light of passing time.

Ehrlich, Eco-Catastrophe, and an Evaluation of Prophecy

"The end of the ocean came late in the summer of 1979. . . . Most of the people who are going to die in the greatest cataclysm in the history of man have already been born." So wrote Paul Ehrlich in *Ramparts* magazine in 1969. Ehrlich, a biology professor at Stanford University, predicted that a new insecticide, more powerful than DDT, would cause disasters in underdeveloped countries. This powerful new chemical would enter the oceans and cause a "massive die-off of sea life." Starvation in nations dependent on seafood would lead to war and the "greatest cataclysm."

Obviously, Ehrlich was wrong. No such superpesticide has been unleashed. And the ocean—although we well might argue about its health—certainly is not dead. What value, then, can be placed on the predictions of such doomsayers? Are Carson, Ehrlich, and others of their ilk merely fools that we may safely ignore and go on our way? Perhaps not. As a result of their warnings, many pesticides have been banned or severely restricted. We have become a good deal more conscious of the



Figure 15.1 Science has thwarted the Malthusian prediction of hunger in the developed countries, but starvation is a fact of life for many people in underdeveloped countries. (Courtesy of the United States Agency for International Development, Washington, D.C.)

environment and our effect on it. Had the Jeremiahs not gained our attention, we might have had an eco-catastrophe. And who knows? Their most horrible predictions, like those of Malthus, may yet come true.

Some Malthusian Mathematics

The basis of Malthus' predictions was some rather simple mathematics. Population, he said, grows geometrically while the food supply is increased arithmetically. In *arithmetic growth*, a constant amount is added during each growth period. As an example, consider a cookie-jar savings account. The first week, little Lavinia puts in the 25¢ she received for her birthday. Each week thereafter, she adds 25¢. The growth of the savings is arithmetic; it increases by a constant amount (25¢) each week. At the end of the first week, she will have 25¢; at the end of the second, she will have 50¢; the third, 75¢; the fourth, \$1.00; the fifth, \$1.25; the sixth, \$1.50; and so on.

Now let's consider an example of *geometric growth*, in which the increment increases in size for each growth period. Again, let's use little Lavinia's bank as an example. The first week she puts in 25¢. The second week she puts in another 25¢, to double the amount (to 50¢). The third week she puts in 50¢, to double the amount again. Each week, she puts in an amount equal to what is already there; she doubles the amount in the bank. At the end of the first week, she has 25¢, the second, 50¢; the third, \$1.00; the fourth, \$2.00; the fifth, \$4.00; the sixth, \$8.00; and so on. Before very many weeks, little Lavinia will have to start robbing banks to keep up her geometrically growing weekly deposits.

Table 15.1 compares arithmetic and geometric growth through 10 growth periods. These data are shown graphically in figure 15.2. Note that arithmetic growth is slow and steady. Geometric growth starts slowly and then shoots up like a rocket.

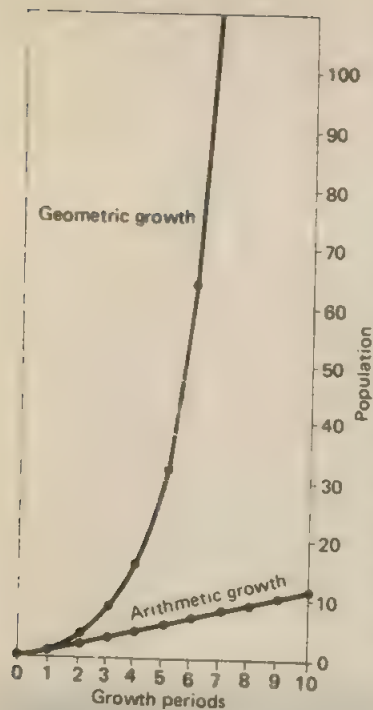


Figure 15.2 A graphic comparison of arithmetic and geometric growth.

Table 15.1
A comparison of arithmetic and geometric growth through 10 growth periods, each starting with a population of one unit

	Growth period										
	0	1	2	3	4	5	6	7	8	9	10
Arithmetic growth	1	2	3	4	5	6	7	8	9	10	11
Geometric growth	1	2	4	8	16	32	64	128	256	512	1024

For a population growing geometrically, we can calculate the *doubling time* from the *Rule of 70*.^{*} Simply divide the percentage of annual growth into 70. The Earth's population is growing 2% per year. If it continues to grow at that rate, the population will double in 35 years. The population of Mexico, growing at 3.5% per year, will double in 20 years.

^{*}The Rule of 70 is derived from the mathematical descriptions of the *rates* of chemical reactions. Its derivation is complex and need not concern us here. (The derivation is discussed in the *Instructor's Guide* for those who are interested.)

What does all this have to do with chemistry? And what does chemistry have to do with agriculture? Well, for one thing, science—with chemistry playing a leading role—made a false prophet of Thomas Malthus, at least for a while. Let's see how it happened. Later on, we look at the prospects for the future.

Plants: Sun-powered Food-making Machines

All food comes ultimately from green plants. As we saw in chapter 8, plants take carbon dioxide and water and, using energy from the sun, reduce these simple compounds to form carbohydrates. With other nutrients, particularly nitrogen compounds, plants can convert the carbon compounds from photosynthesis into **proteins, fats, and other chemicals that we use as food.**

The structural elements of plants—carbon, hydrogen, and oxygen—are derived from air and water. Other plant nutrients are taken from the soil, and energy is derived from the sun. In a primitive society, people grow plants for food. They obtain energy from the food. Nearly all this energy is reinvested into the production of food, although a portion goes into making clothing and building shelter. **Figure 15.3** shows a simplified diagram of the energy flow in a primitive society. Obviously, a real society would be much more complicated than the diagram. Some of the plants, for example, might be fed to animals, and human energy in turn would be obtained from animal flesh or animal products such as milk and eggs.

In primitive societies, nearly all the energy comes from renewable resources. One unit of human work energy, supplemented liberally by energy from the sun, might produce 10 units of food energy. The surplus energy might be used to make clothing or to provide shelter. It also might be used in games or cultural activities.

The flow of nutrients is also rather simple. Unused portions of plants and human and animal wastes are returned to the soil. These are broken down by bacteria, and provide the nutrients for the growth of the new plants (**figure 15.4**). The humus content of the soil is maintained. Properly practiced, this primitive agriculture could be continued for centuries without seriously depleting the soil. The only problem is that farming at that level doesn't support very many people.

Farming with Chemicals: Fertilizers

To replace nutrients lost from the soil and to increase crop production, modern farmers use a variety of chemical fertilizers. The three primary plant nutrients are nitrogen, phosphorus, and potassium. Let's consider nitrogen first.

Nitrogen, though present in air in the elemental form (N_2), is not generally available to plants. There are some forms of bacteria that are able to fix nitrogen, that is, to convert it to a combined, soluble form. Colonies of bacteria that can perform this vital function grow in nodules on the roots of legumes (plants such as clovers and peas). Thus, farmers are able to restore fertility to the soil by crop rotation. A nitrogen-fixing crop (such as clover) is alternated with a nitrogen-consuming crop (such as corn).

Legumes could still be used to supply nitrogen to the soil, and they still are to some extent. But the modern methods of high-yield production demand chemical fertilizers. Why get a corn crop every other year, when you can have one every year?

Plants usually take up nitrogen in the form of nitrate ions (NO_3^-) or ammonium ions (NH_4^+). These are combined with carbon compounds from photosynthesis to form amino acids, the building blocks of proteins (the polymeric compounds essential to all life processes).

For years, farmers were dependent on manure as a source of nitrates. Discovery of deposits of sodium nitrate, called Chile saltpeter, in the deserts of northern Chile led to exploitation of this source as a supplemental source of nitrogen.

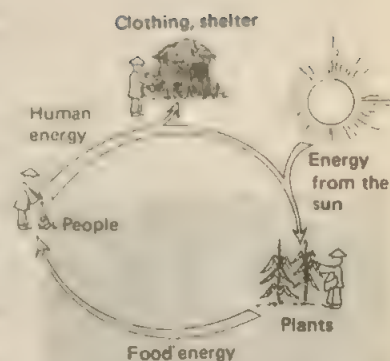


Figure 15.3 Energy flow in a primitive society.

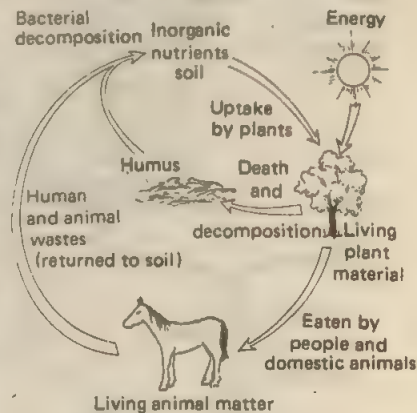
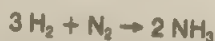


Figure 15.4 Flow of nutrients in a primitive system.

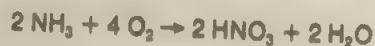
A rapid rise in population growth during the late nineteenth and early twentieth centuries led to increasing pressure on the available food supply. This pressure in turn led to an increasing demand for nitrogen fertilizers. The atmosphere offered a seemingly inexhaustible supply—if only it could be converted to a form useful to humans. Every flash of lightening forms some nitric acid in the air. This process probably contributes about 9 kg of nitrogen per hectare of land per year. Henry Cavendish duplicated this natural process in 1776 by passing an electric spark through a mixture of nitrogen and oxygen, but little came of his achievement.

Nitrates and World War I

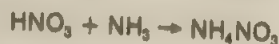
The first real breakthrough in nitrogen fixation came in Germany on the eve of World War I. The process, developed by Fritz Haber, made possible the combination of nitrogen and hydrogen to make ammonia.



By 1913, one nitrogen-fixation plant was in production and several more were under construction. The Germans were able to make ammonium nitrate (NH_4NO_3), an explosive, by oxidizing part of the ammonia to nitric acid.



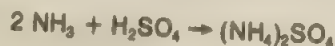
The nitric acid then is reacted with ammonia to produce ammonium nitrate.



The Germans were interested mainly in ammonium nitrate as an explosive, but it turned out to be a valuable nitrogen fertilizer as well. The same discovery that enabled the Germans to prolong World War I probably helped to postpone for several decades Thomas Malthus' predictions of ghastly famine.

Fritz Haber was awarded the Nobel Prize for chemistry in 1918. There are a number of ironies in this. Alfred Nobel, the Swedish inventor and chemist who died in 1896, endowed the Nobel Prize (including the peace prize) with a fortune derived from his own work with explosives. During his lifetime, he was bitterly disappointed by the fact that the explosives he had developed for excavation and mining were put to such destructive uses in war. And Haber, a man who helped his country during World War I, was exiled from his native land in 1933. He was a Jew. Nazi racial laws forced him out of his position as director of the Kaiser Wilhelm Institute of Physical Chemistry. He accepted a post at Cambridge University in England, but his life was ended by a stroke less than a year later.

Increasingly, ammonia is applied directly to the soil as a fertilizer. A gas at room temperature, ammonia is soluble in water and also is easily compressed into a liquid that can be stored and transported in tanks. Much of it, as we mentioned, is converted to ammonium nitrate, a crystalline solid. Some is converted to solid ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ by reaction with sulfuric acid.



These ammonia products can be applied separately or combined with other plant nutrients to make a more complete fertilizer.



Figure 15.5 Fritz Haber, the German chemist who invented a process for manufacturing ammonia. (Courtesy of Encyclopaedia Britannica, Inc., Chicago.)

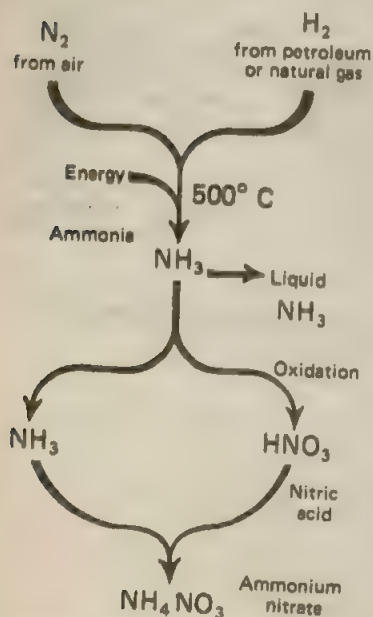
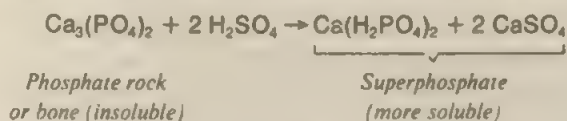


Figure 15.6 Schematic drawing showing how nitrogen fertilizers are made from air and petroleum or natural gas.

It is largely through the use of nitrogen fertilizers that we are able to feed the huge human population that inhabits the Earth. The atmosphere has nearly unlimited nitrogen. Unfortunately, our ways of fixing it require a lot of energy. The hydrogen for synthesis of ammonia comes from natural gas. Petroleum shortages and higher energy prices have led to a scarcity of fertilizers and an inflation of prices. Research is now underway that shows promise for transferring nitrogen-fixing genes to nonlegumes. Perhaps we will soon find a way to fix nitrogen gas at ambient temperatures, the way microorganisms do.

Phosphates: A Legacy from Ancient Life

Animal bones are rich in phosphorus, but the phosphorus is tightly bound and so not readily available to plants. In 1831, an Austrian chemist, Heinrich Wilhelm Köhler, treated animal bones with sulfuric acid in order to convert them to a more soluble form, called superphosphate. In 1843, John Lawes applied the same treatment to phosphate rock. The essential reaction for forming superphosphate is:



Phosphate is quite common in the soil but often at concentrations too low for adequate support of plant growth. Fortunately, there are deposits that are more concentrated. The presence of bones and teeth from early fish and other animals in these ores indicates that the deposits are largely the skeletal remains of sea creatures of ages past. Unfortunately, fluorides often are associated with phosphate ores, and they constitute a serious pollution problem from the production of phosphate fertilizers.

Usually phosphorus is absorbed by plants as H_2PO_4^- . In plants, phosphates are incorporated into DNA and RNA (chapter 11). They also are constituents of compounds essential for the conversion of starches to sugars. Phosphates appear to play a vital role in photosynthesis, mainly by involvement in energy-transfer processes. Phosphorus compounds also are essential to the formation of fats and of some proteins and certain other cell constituents. The availability of phosphorus is often the limiting factor in plant growth.

Phosphates are mined, so they are essentially a nonrenewable resource. Our reserves, it is estimated, will last only about a century or two. Our use of phosphates scatters them irretrievably throughout the environment. Most eventually wind up in the ocean, where they can't be retrieved without an enormous expenditure of energy.

Potassium: The Simple and the Complex

The third major element necessary for plant growth is potassium. Plants use it in the form of the simple ion K^+ . Generally, potassium is abundant, and there are no problems with solubility. The precise function of potassium in plant cells is difficult to determine. It seems to be involved in the formation and transport of carbohydrates. Also, it may be necessary for the buildup of proteins from amino acids.

Uptake of potassium ions from the soil leaves the soil acidic, because each time one potassium ion enters the root tip, a hydronium ion must leave in order for the plant to maintain electrical neutrality (figure 15.7).

The usual chemical form of potassium in commercial fertilizers is potassium chloride (KCl). Vast deposits of this salt occur in Stassfurt, Germany. For years, this source supplied nearly all the world's potassium fertilizer. With the coming of World

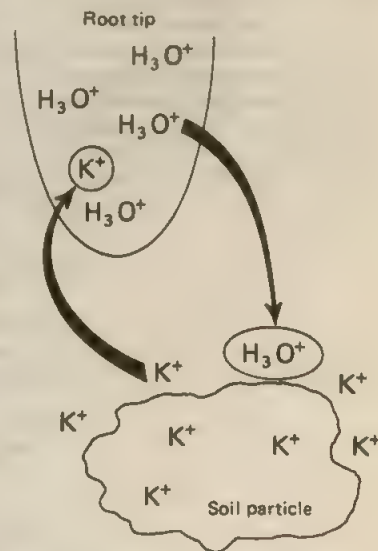
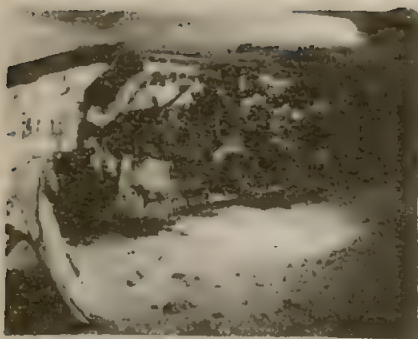


Figure 15.7 When a root tip takes up potassium ions from the soil, hydronium ions are transferred to the soil. Potassium uptake by plants tends to make soil acidic.



(a)



(b)

Figure 15.8 (a) Mining potassium chloride 1.5 kilometres below the prairies of Saskatchewan, Canada. (Courtesy of the Potash Corporation of Saskatchewan.) (b) Mining potash on the surface at the Boulby potash mine, North Yorkshire, England. (Courtesy of Kenneth Warren, University of Oxford.)

War I, the United States sought supplies within its own borders. Deposits at Searles Lake, California, and Carlsbad, New Mexico, now supply much of the United States' needs. Canada has vast deposits in Saskatchewan and Alberta. Beds of potassium chloride up to 200 m thick lie about a kilometre below the Canadian prairies.

Although reserves are large, potassium salts are a nonrenewable resource. They, too, eventually wind up in the ocean. We should use them wisely.

Other Essential Elements

In addition to the three major nutrients, a variety of other elements are necessary for proper plant growth. Three secondary plant nutrients—magnesium, calcium, and sulfur—are needed in moderate amounts. Calcium, in the form of lime (calcium oxide, CaO), is used to neutralize acidic soils.



Calcium ions are also necessary plant nutrients. Magnesium ions (Mg^{2+}) are incorporated into chlorophyll molecules and therefore are necessary for photosynthesis. Sulfur is a constituent of several amino acids, and it is necessary for protein synthesis, including the synthesis of the all-important enzymes (chapter 16).

Seven other elements, called *micronutrients*, are needed in very small amounts. These are summarized in **table 15.1**. Many soils contain these trace elements in sufficient quantity. However, some are deficient in one or more. Production of these soils can be markedly increased by the addition of small amounts of the needed elements.

Table 15.1
Seven micronutrients necessary for proper plant growth

Element	Function	Deficiency Symptoms
Boron	Required for protein synthesis; essential for reproduction and for carbohydrate metabolism	Death of growing points of stems, poor growth of roots, poor flower and seed production
Copper	Constituent of enzymes; essential for reproduction and for chlorophyll production	Twig dieback, yellowing of newer leaves
Iron	Constituent of enzymes; essential for chlorophyll production	Yellowing of leaves, particularly between veins
Manganese	Essential for redox reactions and for the transformation of carbohydrates	Yellowing of leaves, brown streaks of dead tissue
Molybdenum	Essential in nitrogen fixation by legumes and reduction of nitrates for protein synthesis	Stunting, pale green or yellow leaves
Zinc	Essential for early plant growth and maturing	Stunting, seed and grain yields reduced
Chlorine	Increases water content of plant tissue; involved in carbohydrate metabolism	Shriveling

It is possible that other elements also are required by plants. Some elements that may be needed include sodium, silicon, vanadium, chromium, selenium, cobalt, fluorine, and arsenic. Most of these elements are present in most soils. However, their necessity to plant growth has not been established.

Fertilizers: A Mixed Bag

Most farmers buy complete fertilizers, which, despite the name, usually contain only the three main nutrients. There are usually three numbers on fertilizer bags. The first number represents the percentage of nitrogen; the second, the percentage of phosphorus (calculated as P_2O_5); and the third, the percentage of potassium (calculated as K_2O). So 20-10-5 means that the fertilizer contains 20% N, 10% P_2O_5 , and 5% K_2O . The rest is inert material.

Fertilizers must be water soluble in order to be used by plants. When it rains, the nutrients from the fertilizers are washed into streams and lakes, where they stimulate blooms of algae. These chemicals, particularly the nitrates, also penetrate the groundwater. In some areas, the nitrates present in wells have reached levels toxic to babies. These and other water-pollution problems are examined in detail in chapter 18.

Fertilizers have played a vital role in increased food production. We could not begin to feed a hungry world without chemical fertilizers. The Institute of Ecology (reference 11) estimates that the Earth could support only 2 billion people without mined phosphate fertilizers. But the increased production of food has had its price. Among other things, the doubling of food production between 1940 and 1965 required a 600% increase in the use of chemical fertilizers.

The War against Pests: In Days of Old

Since the earliest days of recorded human history (and surely even before that), people have been plagued by insect pests. Three of the 10 plagues of Egypt (described in the Bible, Book of Exodus) were insect plagues—lice, flies, and locusts. The decline of Roman civilization has been attributed in part to malaria, a disease carried by mosquitoes that destroys vigor and vitality when it does not kill. Bubonic plague carried by rats (and by fleas from rats to humans) swept through the Western World repeatedly during the Middle Ages. One such plague (during the 1660s) is estimated to have killed 25 million people—25% of the population of Europe at that time. The first attempt to dig a Panama Canal (by the French during the 1880s) was defeated by an outbreak of malaria.

The use of modern chemical pesticides may be the only thing that stands between us and some of these insect-borne plagues. Pesticides also prevent the consumption of a major portion of our food supplies by insects and other pests. Crop losses to insects in the United States are estimated at \$4 billion a year. When losses to other pests—rodents, fungi, nematodes, and weeds—are included, the losses total \$15 billion a year.

In earlier days, people tried to control insect pests by draining swamps, pouring oil on ponds (to kill the mosquito larvae), and using a variety of chemicals. Most of these chemicals were compounds of arsenic. Lead arsenate [$Pb_3(AsO_4)_2$] is a particularly effective poison, since both the lead and the arsenic in it are toxic. A few pesticides, like pyrethrum (used in mosquito control) and nicotine sulfate (*Black Leaf 40*) are obtained from plant matter.

Only a few insects are harmful. Many are beneficial, and others play important roles in ecological systems and are indirectly beneficial. Most poisons are indiscriminate. They kill all insects, not just those that we consider pests. Most are also toxic to humans and other animals. Some say we should call such poisons *biocides*

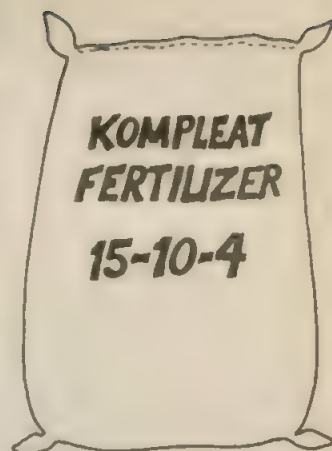


Figure 15.9 The numbers on this bag of fertilizer tell us that the fertilizer is 15% nitrogen (N), 10% phosphorus (as P_2O_5), and 4% potassium (as K_2O).

(because they kill living things) rather than insecticides. Table 15.2 lists the toxicities of some insecticides.

Table 15.2
Toxicity of some insecticidal preparations
administered orally to rats

Pesticide	<i>LD₅₀ (in milligrams of pesticide per kilogram of body weight)</i>
Pyrethrins*	1200
Lead arsenate	800
Carbaryl	540
DDT	113†
Lindane	88
Nicotine sulfate‡	55
Dieldrin	46
Methyl parathion	17
Endrin	8
Parathion	5

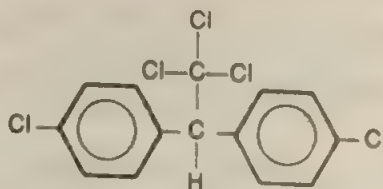
*Active ingredients of pyrethrum.

†Estimated LD₅₀ for humans is 500 mg/kg.

‡Nicotine is much more toxic by injection.

DDT: The Dream Insecticide

Shortly before World War II, a chlorinated hydrocarbon (DDT) was found to be a potent insecticide. The discovery was made in Switzerland by Paul Müller. DDT was tested and found effective against vine grape pests and against a particularly bad infestation of potato beetles.



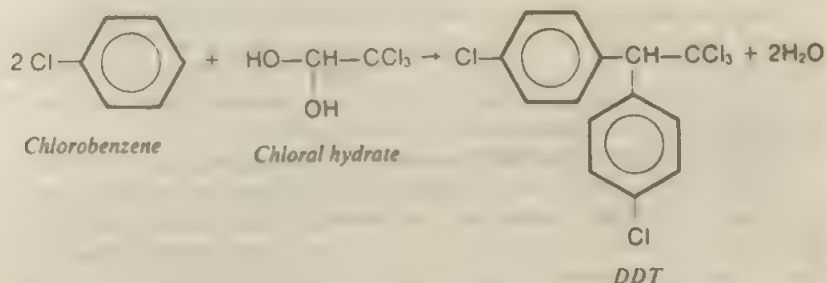
DDT
(dichlorodiphenyltrichloroethane)

When the war came, the supply of pyrethrum was cut off by the Japanese occupation of Southeast Asia and the Dutch East Indies (now Indonesia). Lead, arsenic, and copper compounds, which had been used for insecticides, were needed for armaments and other military purposes. The British and Americans found themselves in need of an insecticide that would protect soldiers from lice and ticks (bearers of typhus). Those who had to fight in the jungles of the South Pacific needed protection from mosquitoes and other disease-bearing pests.

A few pounds of DDT were obtained by the Allies and hurriedly tested. Combined with talcum, it made a very effective delousing powder. Clothing was impregnated with DDT. And, fortunately, it seemed to have no deleterious effects on humans or other large animals. Allied soldiers were virtually free from lice. The

Germans, as they did with the atomic bomb, missed out on DDT even though it was discovered just across their border. German troops were heavily infested with lice and many were sick with typhus. In wars before World War II, more soldiers probably died from typhus than from bullet wounds.

DDT is easily synthesized from cheap, readily available chemicals. Chlorobenzene and chloral hydrate are warmed in the presence of sulfuric acid.



When the reaction is complete, the mixture is poured into water, from which the DDT separates out because, like other chlorinated hydrocarbons, DDT is essentially insoluble in water.

A cheap insecticide, effective against a variety of insect pests, DDT came into widespread use after the war. Other chlorinated hydrocarbons were synthesized, tested, and pressed into service in the war against insects. Although invaluable to farmers in the production of food and fiber, the chlorinated hydrocarbons won their most dramatic victories in the field of public health. According to the World Health Organization, approximately 25 million lives have been saved and hundreds of millions of illnesses prevented by the use of DDT and other chlorinated hydrocarbon pesticides. In India alone, malaria cases were reduced from 75 million to 5 million per year. The average life span in India has been increased by 15 years since the mosquito-eradication program was begun in 1954.

Striking evidence of the value of DDT in public health comes from Sri Lanka (formerly Ceylon), where there were 2.8 million cases of malaria in 1946. By 1963, spraying with DDT had reduced the incidence of malaria to only 17 cases. The spraying program was terminated in 1964, and by 1968, the number of cases had risen to over 1 million per year.

DDT was a dream come true. It seemed that the world would be free at last from insect plagues and insect-borne diseases. Crops would be protected from the ravages of insects and food production would be increased. The Millennium seemed at hand. In recognition of his magnificent discovery, Paul Müller was awarded the 1948 Nobel Prize in medicine and physiology.

Banning a Dream: The Decline and Fall of DDT

Before Müller even received his prize, there were a few warnings that all was not well. Houseflies resistant to DDT were reported as early as 1946. DDT's toxicity to fish was reported by 1947. By 1948, 11 additional resistant species of insects had been discovered. Such early warnings were largely ignored, and it was assumed that the toxicity would disappear soon after the chemical was discharged into the environment. DDT was used extensively to protect crops and control mosquitoes and to try to prevent Dutch Elm disease. Bird populations began to decline in agricultural areas. By 1962, the year Rachel Carson's book *Silent Spring* appeared, United States production of DDT has reached 76 million kg per year.

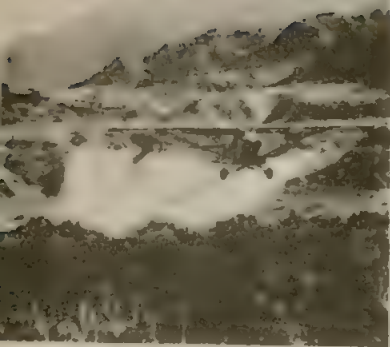


Figure 15.10 The first airplane to land on and take off from the shores of the Dead Sea (24 October 1955) was spraying insecticides against mosquitoes near Gora Sofi, Jordan, as part of a demonstration project sponsored by the United States Department of State in the Middle East, Asia, and Africa. The United States is the major supplier of DDT throughout the world. (Courtesy of the United States Department of Agriculture, Washington, D.C.)

Fish kills, declining bird populations, and a fear of future ecological catastrophes led the United States Environmental Protection Agency to ban the general use of DDT in 1972. Most of the other chlorinated hydrocarbon pesticides have been banned or restricted since then. What made these compounds, once thought to hold such great promise, turn into such villains? Let's examine some of their properties and see whether we can find out.

DDT: Persistence Pays?

One characteristic chemical property of chlorinated hydrocarbons is that they undergo few chemical reactions. They are remarkably stable in the environment. This persistence is a desirable property if you want to kill insects on a crop. DDT stays on the job for weeks or even months. If, on the other hand, you want DDT to stop killing fish, persistence is an undesirable property.

Over 500 million kg of DDT have been introduced into the biosphere. Some of the DDT sprayed from planes is carried into the upper atmosphere, to come down eventually in rainwater in even the most remote places. Traces of the pesticide have been found all over the world, even in Antarctica. The estimated half-life of DDT in the environment is about 15 years. Even though little is used in the United States today, some of the DDT used between 1940 and 1972 will be around in the environment for years.

DDT: Concentration in Fat and Brain

The chlorinated hydrocarbons are only slightly polar. They are insoluble in water but soluble in nonpolar (or slightly polar) substances such as fat. DDT is soluble in fatty tissue. Its lack of water solubility makes it difficult for the body to get rid of.

The fat-soluble nature of DDT causes it to be concentrated in food chains. For example, soil in the Midwest during the mid-1960s was found to contain 9.9 ppm DDT. Earthworms, which obtain their food from decaying organic matter in the soil, were found to have 144 ppm DDT. Robins that ate the worms further concentrated the DDT to 444 ppm, a lethal dose for robins.

Oysters and other shellfish concentrate DDT readily. Many formerly productive coastal areas are completely devoid of valuable seafood resources. Of perhaps greater importance in the long run is the finding that even very small concentrations of DDT (a few parts per billion) interfere with the growth of plankton in the ocean. An increased buildup could convert the seas to deserts devoid of all life, for all other sealife is dependent on plankton at the bottom of the food chain.

Even human fat contains DDT. From a high of about 12 ppm before the ban, the levels had declined to 5.9 ppm by 1973. Even so, if we were cannibals, human flesh could not be sold because of its high DDT content. Mother's milk would be banned for the same reason.

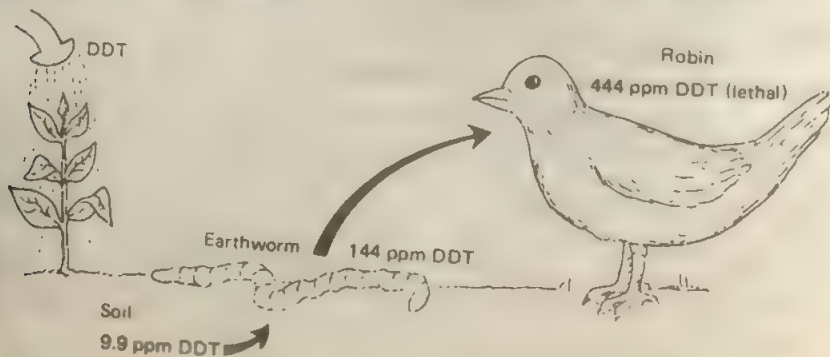
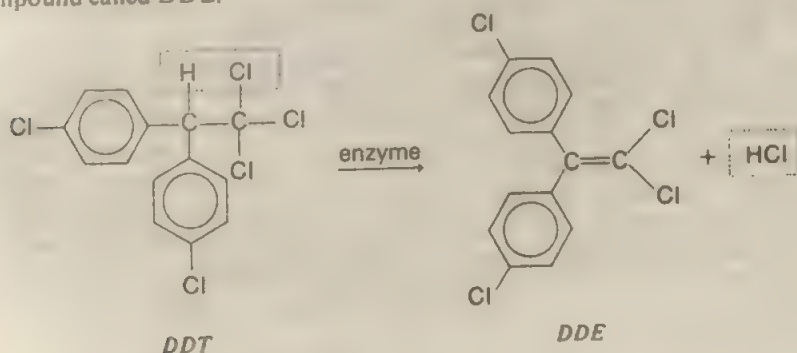


Figure 15.11 A simple food chain showing the increased concentration of DDT from soil to earthworm to robin.

Biochemically, DDT is a nerve poison (chapter 24). DDT concentrates in the fatlike brain tissue. It also interferes with calcium metabolism, essential to the formation of healthy bones and teeth. Although no harm to humans has ever been conclusively demonstrated, the disruption of calcium metabolism in birds has been disastrous for some species. The egg shells, mainly composed of calcium compounds, are thin and poorly formed. The bald eagle, our national symbol, has become an endangered species. The peregrine falcon is nearly extinct. Whole colonies of falcons in which not one egg survived the nesting period unbroken have been observed. If humans reproduced by means of eggs with shells, concern over the effect of DDT would have appeared much sooner.

Insect Resistance: The Insect Dieth Not

Insects often go through several generations in one summer. Genetic change through mutation can be quite dramatic in only a few years. A genetic change in houseflies, leading to the production of enzymes capable of detoxifying DDT, became apparent as early as 1946. The chemistry of one such process shows that the enzyme removes a hydrogen atom and a chlorine atom from DDT molecules to form a compound called DDE.



DDE is less toxic than DDT. Other mechanisms for detoxification are also known now. The destruction of flies with DDT is now virtually impossible in most areas of the world. The resistant variants have survived and multiplied, while those without resistance have been killed off. Most fly populations are now largely made up of resistant flies.

Other insects also have developed resistant strains. In Korea, body lice (carriers of typhus) can no longer be controlled by DDT. Fleas (carriers of bubonic plague) have developed resistance in some areas. Mosquitoes (carriers of malaria and yellow fever) have developed immunity in much of the world. Heavy use of DDT has even resulted in an increase in insect pests brought about by killing off their natural predators. The target pests build up immunity through repeated exposure. The predators concentrate DDT by eating many insects that contain smaller amounts of the insecticide. This leads to interference with the predators' reproductive capacity and even to their deaths.

After the Ban: The Birds Are Back

That nature can recover—at least from the amounts of DDT that have been used to date—is illustrated by the return of robins to the American Midwest. The populations of these harbingers of spring have returned to former levels. Bald eagles and peregrine falcons, although they are still threatened, seem to be making a comeback, too.

The ban on DDT was not a total one. Under certain conditions, it may still be



Figure 15.12 Malaria is controlled in developing countries through the spraying of the walls of houses, where mosquitoes alight after their meal of blood. (Courtesy of the United States Agency for International Development, Washington, D.C.)

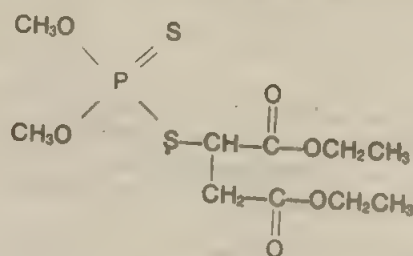
used on three minor crops—green peppers, onions, and stored sweet potatoes. DDT may still be used to protect public health. For example, in case of an outbreak of malaria, DDT could be used to spray mosquito-infested areas. And the *production* of DDT was not banned. It is still produced for export and is exported particularly to developing countries, where it still plays a major role in malaria control (figure 15.12).

The problem of getting a worldwide ban on DDT may solve itself as more and more insect species develop resistance. Its use may be discontinued simply because it is no longer effective. But the need for some type of insect control is apparent, as was dramatically illustrated in Sri Lanka. Chemists, health officials, and agricultural scientists are actively seeking alternatives to DDT and the other chlorinated hydrocarbons.

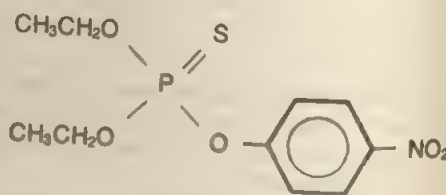
Organic Phosphorus Compounds: More Toxic, Less Persistent

The ban on DDT in the United States has led to the increased use of organic phosphorus compounds. Typical of these compounds are malathion and parathion. Over two dozen of these insecticides are available commercially (reference 5). They have been extensively studied and evaluated for effectiveness against insects and for toxicity to people, laboratory animals, and farm animals.

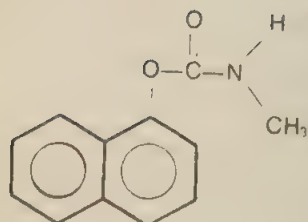
The organic phosphorus compounds are generally much more toxic to mammals than are the chlorinated hydrocarbons. Table 15.2 shows that parathion is over 20 times as toxic to rats as is DDT (a smaller LD_{50} means greater toxicity). Dozens of farm workers have been killed by these potent poisons. However, organic phosphorus compounds break down rapidly in the environment. Unlike what happens with DDT, residues are seldom found in food. However, agricultural leaders have expressed the opinion that we may have gained safety for the peregrine falcon and the bald eagle at the expense of the farm workers.



Malathion



Parathion

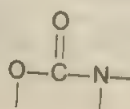


Carbaryl
(Sevin)

Carbamates: A Honey of An Insecticide?

Another class of compounds that has gained prominence since the ban on DDT is the carbamates. Typical examples are carbaryl (*Sevin*) and carbofuran (*Furadan*). Carbamates generally have low toxicity to mammals and are fairly effective against a variety of insect pests. They also break down rapidly in the environment. Unfortunately, carbaryl is particularly toxic to honeybees. Millions of these valuable insects have been wiped out by spraying crops with carbaryl.

The essential feature of the carbamate molecule is the group



Many variations are possible by changing the groups attached to the oxygen and the nitrogen. Several carbamates have achieved commercial importance. Research continues in an effort to develop more effective carbamate insecticides. The future, however, may belong to alternatives to the synthetic chemical pesticides.

The Sex Trap: Pheromones

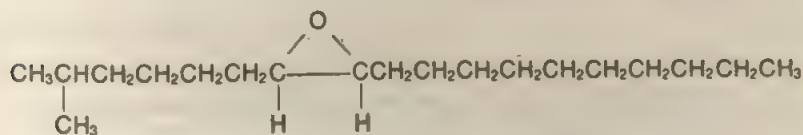
One of the most promising areas of research in insect control is the research into pheromones. These interesting chemicals are secreted externally by insects and may serve the function of marking a trail, sending an alarm, or attracting a mate. Perhaps the most interesting pheromones are the insect sex attractants which usually are secreted by the female to attract males. Chemical research can identify the sex attractants and determine their structures. These compounds then can be synthesized and used to lure males into traps. Alternatively, the attractant can be used in quantities sufficient to confuse and disorient the males, who detect a female in every direction but can't find one to mate with.

Some sex attractants are amazingly simple. Others are complex. The sex attractant for the common housefly is a simple unsaturated hydrocarbon.



Although this molecule contains 23 carbon atoms (with a double bond between the ninth and tenth), it is fairly easy to synthesize. Quantities of it are now available for testing and development.

However, most research in sex attractants is not easy. Some pheromones have rather complicated structures. All are secreted in extremely tiny amounts. For example, a team of United States Department of Agriculture researchers had to use the tips of 87 000 female gypsy moths to isolate a minute amount of a powerful sex attractant. The structure of the compound was determined by using a variety of sophisticated instruments. It was found to be:



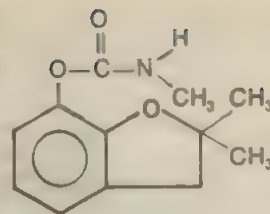
The compound was first isolated in 1967, but it was not until 3 years later that the group had synthesized it in the laboratory. Field tests showed the synthetic attractant to be effective in concentrations as low as 0.000 000 000 001 g (10^{-12} g) in baited traps.

Perhaps the best use of sex attractants would be to use them in traps that monitor insect populations. Synthetic chemical pesticides then could be used with maximum effectiveness.

A variety of pheromones have been isolated, identified, and synthesized. Much work remains to be done, however, before this very specific form of insect control can replace effectively the broad-spectrum insecticides. The method is expensive; research is painstaking and time-consuming. Workers must be careful not to get the attractants on their clothes. Who wants to be attacked on a warm summer night by a million sex-crazed gypsy moths?

Biological Controls: Fighting Bugs with Bugs

Another promising avenue of research is in the use of natural enemies to control pests. Praying mantises and ladybugs are sold commercially and are used to destroy garden pests. Biological controls also include bacteria and viruses, often specific for



Carbofuran
(Furadan)



Figure 15.13 A male gypsy moth detects odor from a female by using his large antennae. (Courtesy of the United States Department of Agriculture, Washington, D.C.)

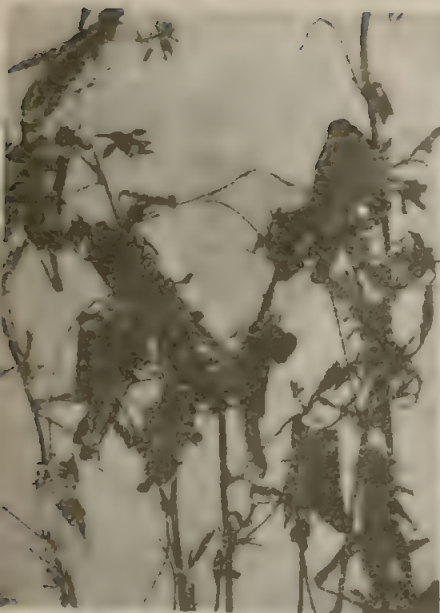


Figure 15.14 Grasshoppers killed by a viral insecticide. (Courtesy of the United States Department of Agriculture, Washington, D.C.)

a given species of pest. Bacteria have been used successfully to combat termites in the tropics. When these insects are found, they are treated with bacteria, which they then carry back to their nests, infecting whole colonies.

Viruses have been tested successfully against a number of insect pests. Final approval was given in 1972 for the use of a virus as a pesticide directed against *Heliothis zea*, a remarkable pest that is known by a variety of aliases—cotton bollworm, corn earworm, tobacco budworm, and tomato fruitworm—depending on the crop that it's attacking. The virus is cultured in a "factory," which will be able to supply enough virus to treat a substantial portion of the United States cotton crop. Viral pesticides also show promise against grasshoppers (figure 15.14) and many other insect pests.

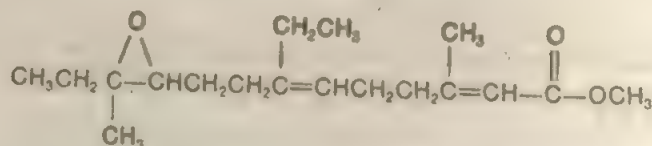
Production of viral pesticides is expensive. Nevertheless, this approach to insect control is intriguing, because viral agents are highly specific, nontoxic to people and other animals, and completely biodegradable.

Another biological approach is the breeding of insect- and fungus-resistant plants. Such plants, particularly grain bearers, have contributed considerably to the increased crop production in recent years.

Juvenile Hormones: Why Don't You Never Grow Up?

Another approach to insect control is the use of juvenile hormones. Hormones are the chemical messengers that control many life functions in plants and animals. Minute quantities produce profound physiological changes. In the insect world, juvenile hormones control the rate of the development of the young. Normally, production of the hormone is shut off at the appropriate time to allow proper maturation to the adult stage.

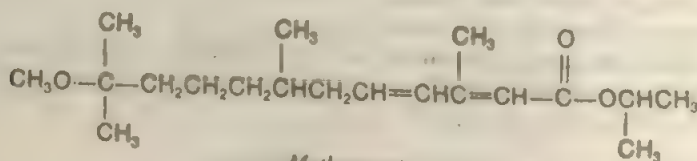
Chemists have been able to isolate a variety of insect juvenile hormones and determine their structure. With knowledge of the structure, they then can synthesize the hormone. A mosquito juvenile hormone has been isolated and its structure determined.



A mosquito juvenile hormone

Application of this hormone to the ponds where mosquitoes breed keeps mosquitoes in the harmless larval stage. Since only adult insects can reproduce, juvenile hormones appear to be a nearly perfect method of mosquito control.

Chemists even have been able to improve on nature by synthesizing even more effective compounds. Methoprene, an analog of the mosquito juvenile hormone, has been developed.



Methoprene

It was approved by the United States Environmental Protection Agency in 1975 for use against mosquitoes.

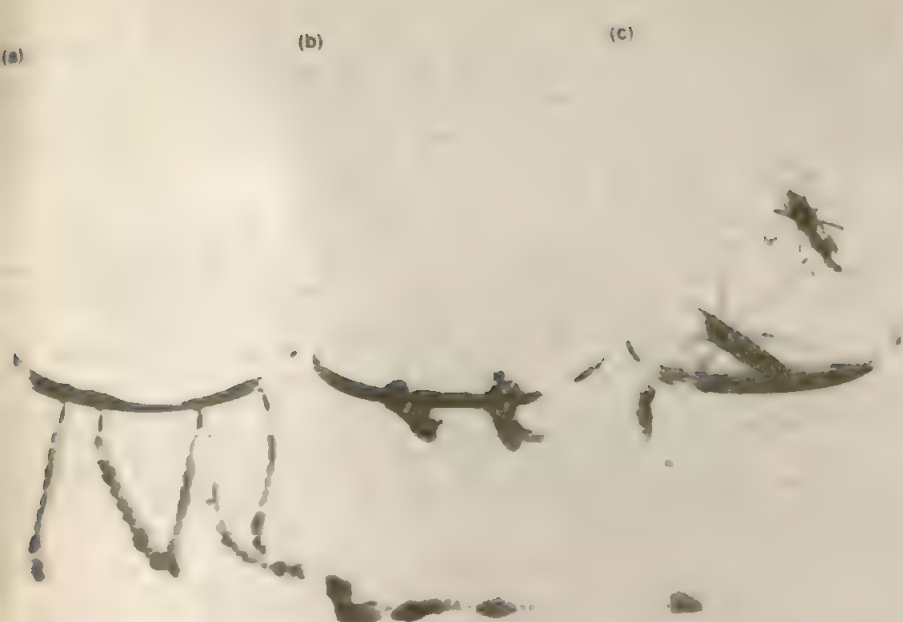


Figure 15.15 The use of juvenile hormones in pesticides like methoprene can prevent mosquitoes from maturing. (a) Mosquito larvae. (b) Mosquito larvae trapped in pupae stage. (c) Adult mosquitoes. (Courtesy of Manufacturing Chemists Association, Washington, D.C. Reprinted from *ChemEcology*, May 1975.)

Juvenile hormones are difficult to synthesize (as you could probably guess from their complex structures) and consequently are quite expensive. They are effective mainly for use against insects that are pests at the adult stage. Little would be gained by keeping a moth or a butterfly in the caterpillar stage for a longer period of time; caterpillars have voracious appetites and do a great deal of damage to crops. The damage these larvae could do might not be compensated by their lack of reproduction.

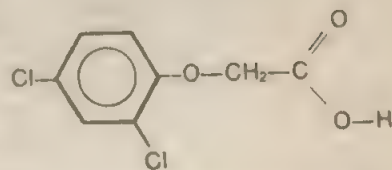
Sterilization: Once Is Enough

A technique effective on insects that breed only once per season is sterilization. Large numbers of males are sterilized by radiation, chemicals, or crossbreeding. So many of them then are released that they far outnumber the local fertile males. Once a female has mated, that's it. If she has met with a sterile male, no offspring are produced.

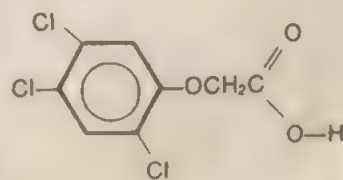
Radiation sterilization has virtually eliminated the screwworm fly, once a serious pest that affected cattle in the southern United States. Tropical fruitflies also have been eradicated by this method in some areas. However, results with other pests have been disappointing. The search goes on for effective ways to control insects and thus protect us from disease and prevent damage to our food supply.

Herbicides and Defoliants

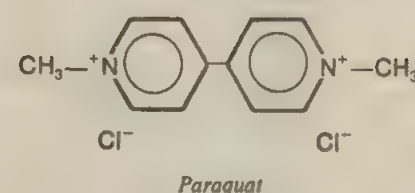
Crops produce more abundant harvests when they have no competition from weeds. Removing the weeds by hand is tedious, back-breaking work. Chemical herbicides have been used for a number of years to kill the unwanted plants. Solutions of copper salts, sulfuric acid (H_2SO_4), and sodium chlorate (NaClO_3) have been used, but it wasn't until the introduction of 2,4-D in 1945 that the use of herbicides became common. Chemically, 2,4-D is 2,4-dichlorophenoxyacetic acid or one of its derivatives. These chemicals are growth-regulator herbicides and are especially effective against newly emerged, rapidly growing broad-leaved plants. A relative of 2,4-D, called 2,4,5-T, is especially effective against woody plants; it works by causing the leaves to fall off the plants (*defoliation*).



2,4-Dichlorophenoxyacetic acid
(2,4-D)



2,4,5-Trichlorophenoxyacetic acid
(2,4,5-T)

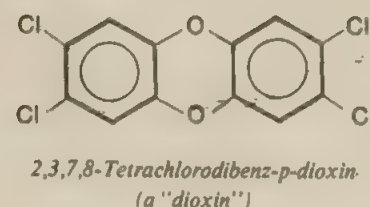
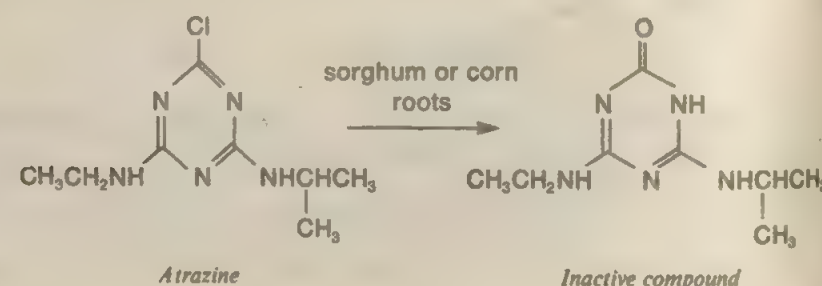


There is no doubt that the use of herbicides has increased the value of agricultural crops by billions of dollars. Roadsides, vacant lots, and industrial areas also have been kept free of weeds. People who suffer from allergies caused by pollen from ragweed and other plant pests have been relieved, and poison ivy and other toxic weeds have been made less common.

Chemical defoliants also have been used for years, generally to facilitate the harvesting of crops. Calcium cyanamide (CaNCN) was one of the earliest defoliants used for this purpose. It causes cotton plants to lose their leaves when the bolls are mature, thus making possible the use of mechanical cotton pickers. If the leaves were left on, they would be crushed by the machinery and stain the cotton green.

Another type of herbicide includes the preemergents, such as paraquat. This ionic compound is toxic to most plants, but it is rapidly broken down in the soil. Therefore, paraquat can be used to kill weed plants before the crop seedlings emerge.

Atrazine is an example of still another type of herbicide. It kills most plants by blocking a key step in photosynthesis. Corn and sorghum are able to deactivate atrazine, however. Root cells in these plants convert the herbicide to an inactive compound.



Thus, atrazine can be used to kill weeds without harming the corn crop.

Herbicides generally have a better safety record than insecticides. Only a rather severe problem has been noted. 2,4,5-T preparations have been implicated in causing serious birth defects in laboratory animals. The birth defects have been shown to be caused by a contaminant, called a *dioxin*, and not by 2,4,5-T itself. Careful controls in the manufacture of this herbicide should eliminate this hazard in the future.

The Antichemical Revolt: Organic Farming

Problems with pesticides have led to a minor resurgence of organic farming. Many people hold that we can have more nutritious food and avoid environmental problems by banning chemical pesticides and fertilizers and growing crops the natural way.

The movement is admirable in many respects. It seems rather evident that we should return human and animal wastes to the soil rather than polluting our water and air with them. Organic farming also is less energy intensive. According to a study by the Center for the Biology of Natural Systems at Washington University, the comparable conventional farms use 2.3 times as much energy as organic farms. Production on the organic farms was 10% lower, but costs were lower by a comparable percentage. Organic farms require 12% more labor than conventional ones, but human labor is a renewable resource, whereas petroleum energy is not.

Most likely, we should practice organic farming to the limit of our ability to do so. But we should not delude ourselves. Despite claims to the contrary, organically grown food has not been shown to be more nutritious than food grown with modern

techniques. Chemical analysis can detect no difference between food organically grown and food produced by using chemical fertilizers. And organic fertilizers must be broken down to inorganic chemicals before they can be utilized by plants.

Energy and Agriculture

Modern agriculture is energy intensive. Nonrenewable petroleum energy is required for the production of fertilizers and pesticides and farm machinery. Energy is required to run the machinery used for tilling, harvesting, and transporting crops. It also takes energy to process and package our food (figure 15.16).

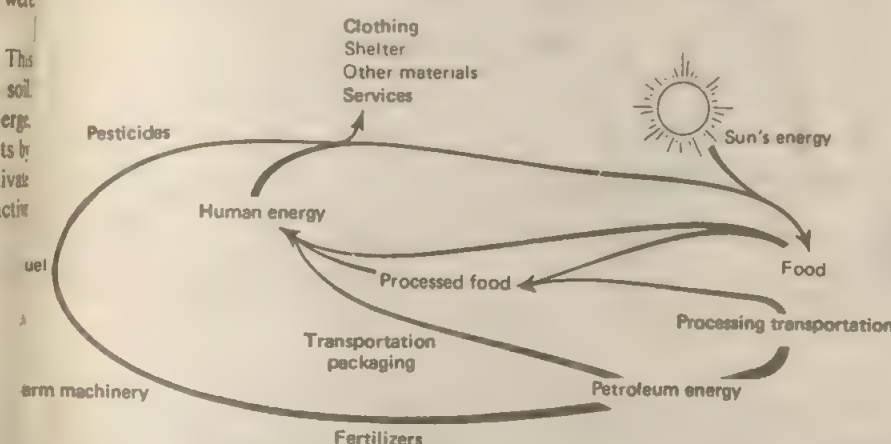


Figure 15.16 Energy flow in modern agriculture.

It is estimated that 10 units of petroleum energy are required to produce 1 unit of food energy. Increasing energy prices may well force us to reevaluate our farming methods. If we consider production per hectare, modern farming is marvelously efficient. If we consider the energy used in relation to the energy produced, it is remarkably inefficient. It should be noted, however, that in an energy efficient, primitive society, nearly all human energy goes into food production. In modern societies, only about 10% of our energy is devoted to producing food. The other 90% is used to provide the materials and services that are so much a part of our civilization. We should try to make our food production more energy efficient, but it is unlikely that we will want to return to a primitive way of life.

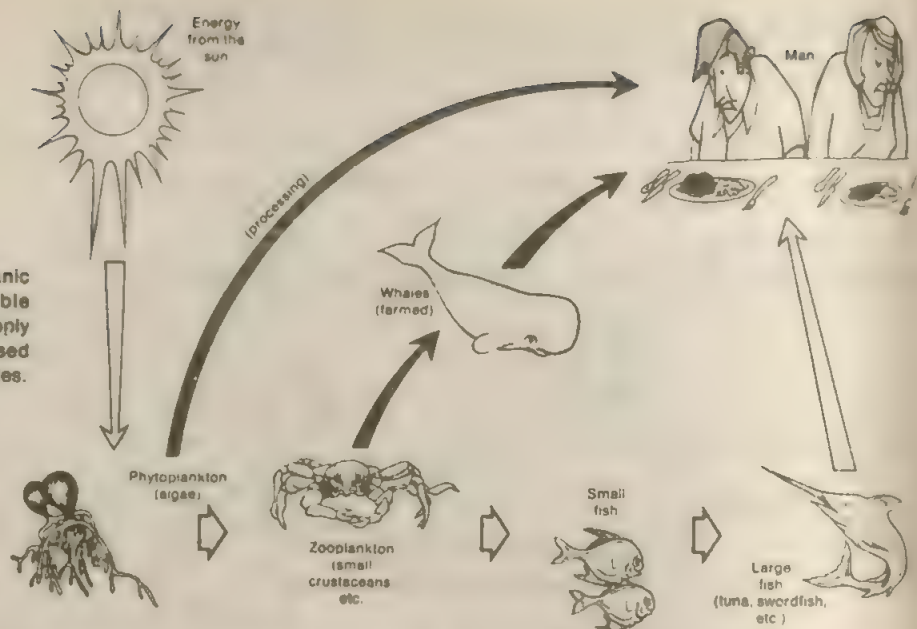
Can We Feed a Hungry World?

The population of the Earth reached 4 billion in 1976. At a growth rate of 2%, it will reach 8 billion in 2011. Will we be able to feed all those people?

Agriculture in developed countries is heavily dependent on petroleum energy. The pesticides and fertilizers derived from petroleum. New plant species have been developed, but these crops require increased amounts of pesticide and fertilizer.

There are other possible ways to stretch our food supply. Production of protein from petroleum was shown by 1970 to be not only possible but economically feasible. Certain varieties of yeasts, when mixed with oil and supplied with the proper mineral nutrients, were able to convert the hydrocarbons of the oil to proteins. To date, problems with the product's oily taste and residual toxicity have prevented these proteins from being an important source of food for humans. Besides, we have a shortage of petroleum for fuel and petrochemicals. It is unlikely that we will divert a substantial portion of it to the production of proteins.

Figure 15.17 A simplified oceanic food chain showing two possible shortcuts to an increased food supply for humans: (1) eating processed algae and (2) eating "farmed" whales.



Some people have speculated on the possibility of harvesting algae from the oceans and processing it for human consumption. This shortening of the food chain (figure 15.17) would eliminate the highly inefficient steps in the predator-prey relationships in the food cycle and would enable us to live directly off the organisms that capture energy from the sun—the algae. Another scheme, the farming of whales, also would reduce the number of steps in the food chain.

Any schemes like these would have to contend successfully with the problem of inducing people—even hungry people—to eat unfamiliar foods. And, as for whales, instead of farming them, we are rapidly killing off these giant ocean mammals. Some species have been hunted to near extinction. And the oceans are being rapidly fished out, and the pollution of the seas is increasing. It seems obvious that we cannot use the oceans both as sources for additional food supplies and as dumps for increasing amounts of poisonous and radioactive wastes.

Figure 15.18 shows the relationship between arable land available for food production and population. Even by quadrupling present food production, we could meet our needs only until 2050. Since virtually all the world's arable land is now under cultivation, it should be quite evident to everyone that food production cannot keep up for long with the present rate of population growth.

We seem to be hooked on a high-energy form of agriculture that uses synthetic fertilizers, pesticides, and herbicides and depends on the power of machinery that burns fossil fuels. Ultimately, the only solution to the problem is population control. Obviously, that will come some day. The only questions are when and how. Population control could come through decreasing the birthrate. This could happen voluntarily, but that involves education and cultural change, both usually very slow. It could come through governmental control, but with over 100 sovereign governments in the world such control seems unlikely to be effective. The other possibility for population control is an increase in the deathrate—through catastrophic war, famine, pestilence, or the poisoning of the environment by the wastes of an ever-expanding population. The ghost of Thomas Malthus haunts us yet.

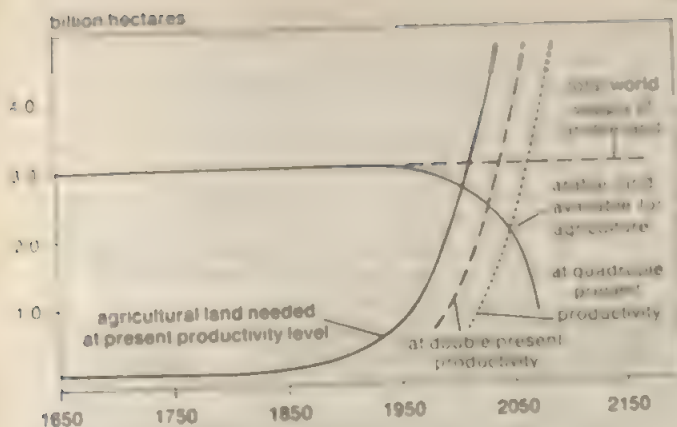


Figure 15.18 The total supply of available land is fixed. Continued population growth threatens to outstrip even the most optimistic projections of food production.

Problems

- The populations of some Latin American, African, and Asian nations are growing at 1.5% a year. At that rate, how many years of growth will it take for those populations to double?
- Discuss the advantages and the disadvantages of each of the following methods of insect control.
 - persistent pesticides (e.g., DDT)
 - organic phosphates (e.g., parathion)
 - sex attractants
 - natural enemies
 - juvenile hormones
 - sterilization
- What are the advantages of organic farming? The disadvantages?
- If you were to grow a garden, would you use chemical fertilizers? Pesticides? Why or why not?
- How much DDT would it take to kill a person weighing 60 kg if the lethal dose were 0.5 g per kilogram of body weight?
- How much parathion would it take to kill the person in problem 5 if the lethal dose were 5 mg per kilogram of body weight? How much Soman if the lethal dose were 0.01 mg per kilogram of body weight?
- Discuss the possibilities of increasing our food supplies by each of the following.
 - farming the seas
 - converting petroleum to protein
 - genetic engineering
 - using other methods
- What are the three major plant nutrients? What is the role of each in plant nutrition?
- What are the three secondary plant nutrients? What is the role of each in plant nutrition?
- List three (of the seven) plant micronutrients. What is the role of each in plant nutrition?
- Compare organic farming with conventional farming with regard to energy requirements, labor, profitability, and crop yields.
- Examine the label on a package of yard or garden pesticide. List its trade name and active ingredients.
- Examine the label of a bag of fertilizer. What is its composition?
- List four alternatives to chemical pesticides. Describe how each works. Why are they not in widespread use?
- Where does most of the matter of a growing plant come from?
- Describe how chlorinated hydrocarbon pesticides become concentrated in a food chain.
- Use a reference such as *The Merck Index* (reference 21) to look up each of these pesticides. What is the toxicity of each?

a. methoxychlor	d. dieldrin	g. kepone
b. lindane	e. heptachlor	h. toxaphene
c. aldrin	f. mirex	i. endrin

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chapter 16

Food: Those Incredible Edible Chemicals

Life is sustained by a complex set of chemical processes. Food is the group of chemical reagents that take part in the life-sustaining processes. Food supplies the materials from which living organisms are made. Food supplies the energy that keeps organisms alive. Food furnishes the parts for the growth and repair of tissues. Without food, we would die in a few weeks.

In much of the Western World, the problem often is an overabundance of food. We eat too much food—and often the wrong kinds of foods. It is estimated that over 30% of the adults in the United States are overweight. Obesity contributes to poor health: increased risk of cardiovascular disease and diabetes and perhaps increased susceptibility to other diseases as well. An obese person also has a shorter life expectancy than a person of average weight. Our diet (which is too rich in fat, sugar and salt) has been linked to 6 of the 10 leading causes of death in the United States.

In developing countries, the problem often is too little food or food of inadequate quality. Malnourished children, particularly, are more susceptible to disease. They often die of chicken pox and measles, diseases that present little threat to healthy children. Inadequate food leaves children small in stature and stunted mentally. They need more and better food to become strong in body and mind.

Just as life is a lot more than the sum of a set of chemical processes, food is more than just a collection of chemicals. Food often is consumed on social occasions, and it can't be separated from its cultural context.

Chemicals Eat Chemicals

The human body is a conglomeration of chemicals. If we did a chemical analysis of the human body, we would find that it is largely water, about 60%. There are a number of minerals present, also. The blood and the other body fluids contain dissolved salts. The bones and teeth are similar to hydroxyapatite, a mineral found in phosphate rock. A little glucose ($C_6H_{12}O_6$, a simple sugar) is found in the blood. There is fat under the skin and around the internal organs. A form of starch (glycogen) is found in the liver and in the muscles. And, in every cell of the body,

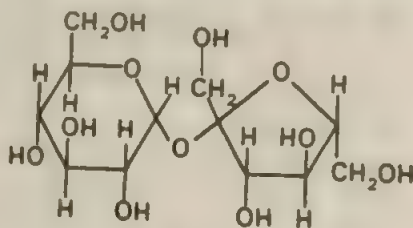
there are proteins. There are also thousands of other chemicals that play vital roles in the life processes of the human body.

We need food for growth when we are children. At all ages, we need food for the replacement and repair of tissues, and we need food for energy. Normally, these needs are met by the foods we eat. The three main classes of foods used by people and other animals are carbohydrates, fats, and proteins. These, too, are chemicals. For proper nutrition, our diet should consist of balanced proportions of all three types of foods, plus vitamins, minerals, and dietary fibers. In the remainder of this chapter, we see how each of these substances fulfills its function in our bodies.

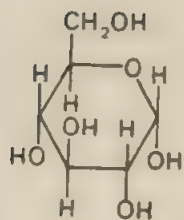
Carbohydrates: Our Storehouse of Energy

Carbohydrates are compounds of the elements carbon, hydrogen, and oxygen. Usually, the atoms of these elements are present in a ratio expressed by the formula $C_n(H_2O)_n$. Glucose, which has the formula $C_6H_{12}O_6$, could be written $C_6(H_2O)_6$. Indeed, it is from formulas such as these that the term *carbohydrate* is derived. We use it even though the term is misleading; carbohydrates are not hydrates of carbon.

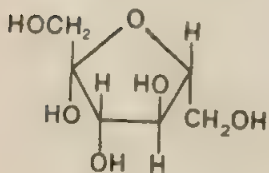
Sugars, starches, and even celluloses are carbohydrates. Sugars have been used for ages to make certain foods sweeter and so more palatable. Common table sugar is sucrose ($C_{12}H_{22}O_{11}$), derived principally from sugarcane and sugar beets. Per capita consumption of sugar in the United States is about 45 kg per year. Much of it is consumed in soft drinks, presweetened cereals, and other highly processed foods with little or no other nutritive value. The empty calories from sweetened foods contribute greatly to tooth decay, obesity, and heart disease.



Sucrose



Glucose (dextrose)



Fructose

Some food faddists claim that raw sugar is much better for you than refined sugar. Actually, raw sugar does contain a few trace minerals but hardly enough to make it a lot more desirable than refined sugar. Raw sugar is still mainly sucrose, and, if sucrose is harmful, a few impurities in it won't make it less so. People in many of the developed countries probably consume much too much sugar—raw or refined.

Sucrose is broken down in our bodies to two simpler sugars, glucose and fructose. Glucose (also called dextrose) is the most common simple sugar used by the cells of our bodies for energy. Glucose is the simple sugar that is circulated in the bloodstream; that is why it is sometimes called *blood sugar*. Fructose occurs in many fruits; sometimes it is called *fruit sugar*.

Corn syrup, an increasingly important sweetener, is mainly glucose. It is made by the hydrolysis of starch. Honey also is a popular sweetener. It is for the most part a mixture of glucose and fructose. Some food faddists attribute special nutritive value to honey. It does have a few vitamins and minerals but not enough to make it much better than other sugar sources as far as nutrition is concerned. Sugar is sugar. No matter what form of sugar we eat, it is converted to glucose for use by our cells.

As foods, complex carbohydrates have a somewhat better reputation than the

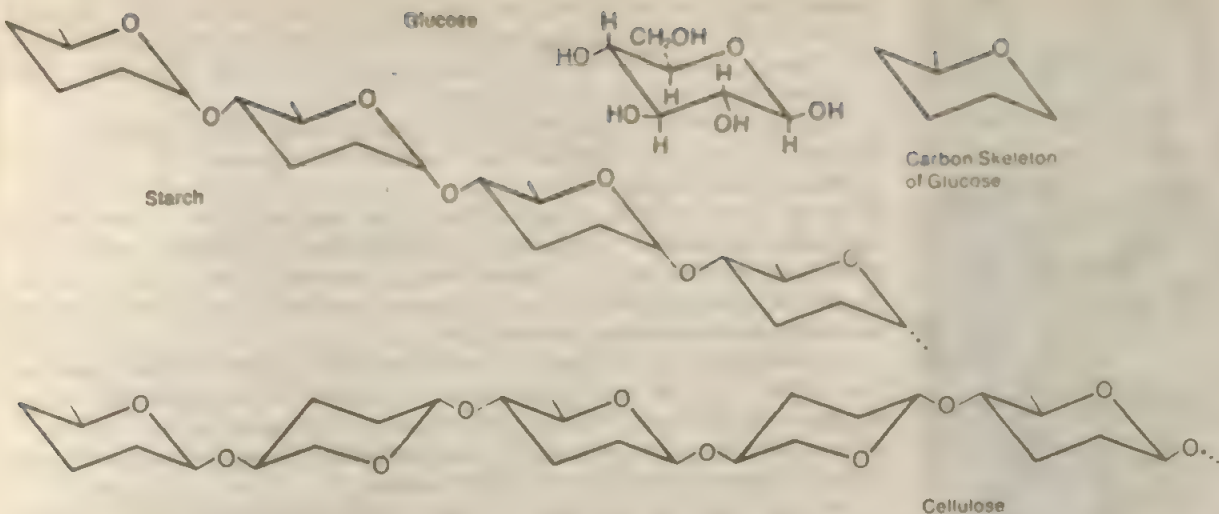


Figure 16.1 Carbohydrates Both starch and cellulose are polymers of glucose

simple sugars. Starch is an important part of any balanced diet. Cellulose contributes fiber to our diet.

The carbon skeleton of part of a starch molecule is shown in **figure 16.1**. Notice that starch is a polymer of glucose. Cellulose is also a polymer of glucose. The main structural difference between starch and cellulose is in the way the glucose units are hooked together in them. This may seem to be a minor difference, but all animals can digest and metabolize starch while humans and most other animals get no food value from cellulose. Bacteria in the digestive tract enable grazing animals and termites to utilize cellulose.

Different linkages also result in different three-dimensional forms for cellulose and starch. For example, cellulose in the cell walls of plants is arranged in *fibrils*, bundles of parallel chains. The fibrils, in turn, lie parallel to each other in each layer of the *cell wall* (**figure 16.2**). In alternate layers, the fibrils are perpendicular, this imparts great strength to the cell wall.

The glycogen (animal starch) in muscle and liver tissue is arranged in granules (**figure 16.3**). These granules are clusters of small particles. Plant starch, on the other hand, forms large granules. Plant starch granules rupture in boiling water to form a paste. On cooling, the paste gels. Potatoes and cereal grains, when cooked in water, form this type of starchy broth.

Starch is broken down to glucose when it is digested. This simple sugar is readily absorbed through the intestinal walls and taken into the bloodstream. The body then metabolizes this glucose, using it as a source of energy. Glucose is broken down through a complex set of more than 50 chemical reactions to produce carbon dioxide and water, with the release of energy.



These reactions are essentially the reverse of photosynthesis. In this way, animal organisms are able to make use of the energy from the sun that was captured by plants in the process of photosynthesis.

The steps in this complicated process are catalyzed by *enzymes*, protein molecules that enable the reactions to occur at convenient rates at much lower temperatures than they would otherwise. Each step involves only a small energy

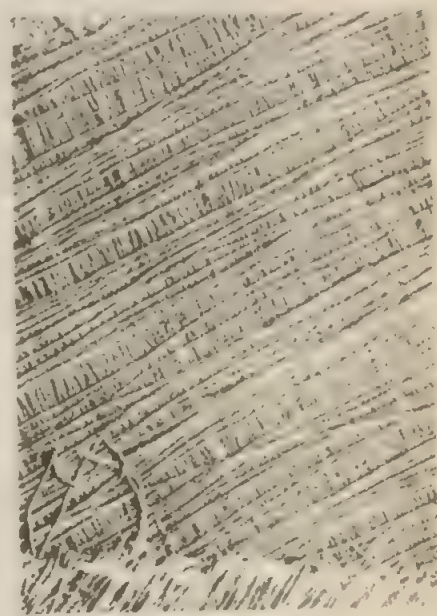


Figure 16.2 Electron micrograph of the cell wall of an alga. The wall consists of successive layers of cellulose fibers in parallel arrangement. (Photo by R. D. Preston, F.R.S., and E. Frei.)

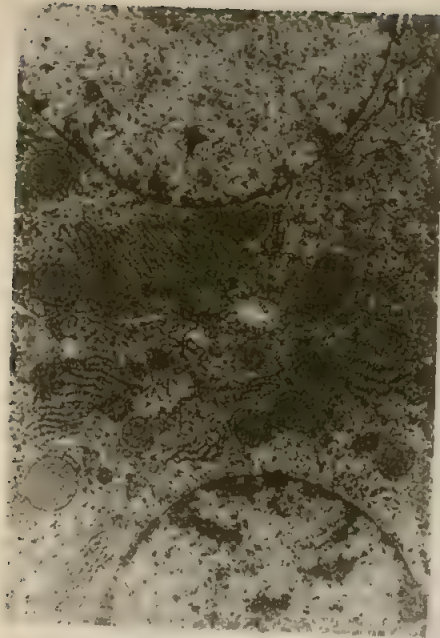


Figure 16.3 Electron micrograph of glycogen granules in a liver cell of a rat. (Photo by Patricia J. Schulz.)

change, whereas the overall reaction releases a large amount of energy. We could obtain the same amount of energy by burning the glucose at elevated temperatures in air without enzymes, but the temperature required and the heat produced in the more direct process would destroy living cells.

Enzymes seem to operate by a sort of lock-and-key effect (**figure 16.4**). The enzyme for a particular reaction must fit precisely the molecule it is acting upon. Enzymes that break down starch to glucose don't fit the cellulose molecule (note the difference in the way the glucose units are linked together in the two polymers in **figure 16.1**, so cellulose can't be metabolized by animal organisms. Some bacteria (such as those inhabiting the digestive tracts of ruminants and termites) do have enzymes for breaking down cellulose to glucose, so these bacteria (and their hosts) are able to obtain food value from cellulose.

Carbohydrates are quick-energy foods. They supply about 4 kcal of energy per gram. (The kilocalorie often is simply called a Calorie when used to describe the energy content of foods.) When we eat more than we can use, a small amount of carbohydrate can be stored in our liver and muscle tissue as glycogen. Large excesses, however, are converted to fat for storage.

A proper diet should be about 65% by weight carbohydrate. Potatoes, breads, cereals, and some fruits are good sources of carbohydrates.

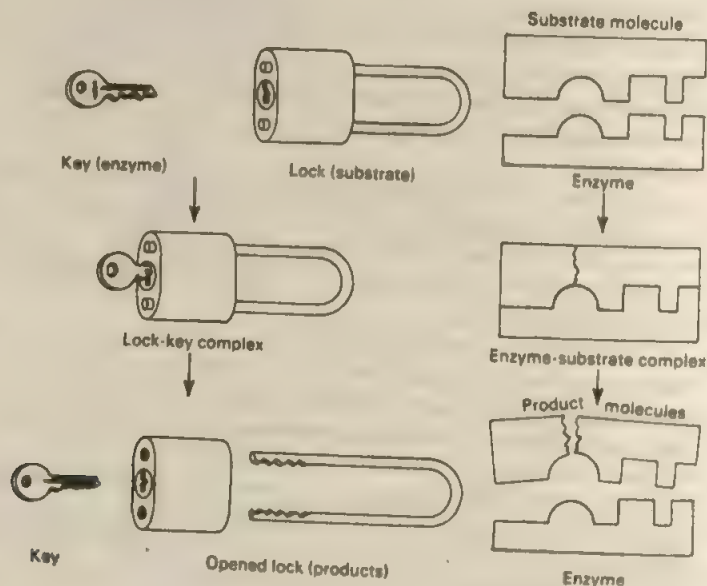
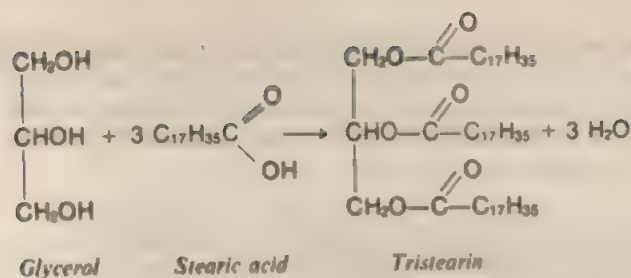


Figure 16.4 Lock-and-key model of enzyme action.

Fats: Padding, Insulation, and Reserve Energy

Like carbohydrates, fats are compounds of the elements carbon, hydrogen, and oxygen, but they are quite different from carbohydrates. Fats are *esters* (chapter 11). They can be thought of as being derived from the trihydroxy alcohol glycerol and long-chain carboxylic acids (*fatty acids*).

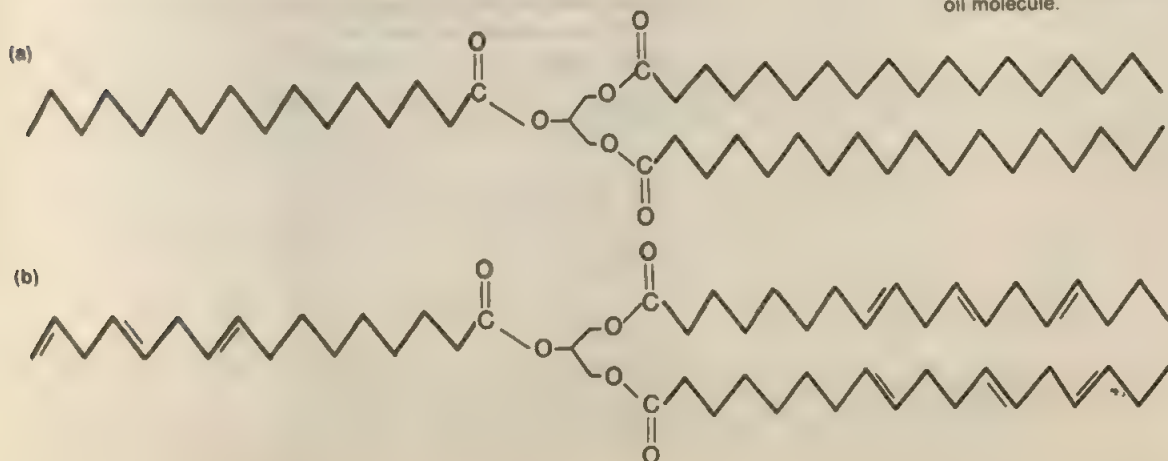


Naturally occurring fatty acids nearly always have an even number of carbon atoms. Representative ones are listed in **table 16.1**. Solid fats, such as lard, are esters of glycerol and saturated fatty acids. Liquid fats are called *oils*. Structurally, these oils are glyceryl esters of unsaturated fatty acids. Cottonseed, peanut, corn, linseed, and olive oils are familiar liquid fats. Carbon skeletal structures of a typical saturated fat molecule and of an unsaturated oil molecule are shown in **figure 16.5**. Keep in mind that, in this type of representation, each corner represents a carbon atom, and each carbon atom would have enough hydrogens attached to give it a total of four bonds.

Table 16.1
Some fatty acids in natural fats

Number of Carbon Atoms	Condensed Structure	Name	Source
4	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	Butyric acid	Butter
6	$\text{CH}_3(\text{CH}_2)_4\text{COOH}$	Caproic acid	Butter
8	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$	Caprylic acid	Coconut oil
10	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$	Capric acid	Coconut oil
12	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	Lauric acid	Palm kernel oil
14	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	Myristic acid	Oil of nutmeg
16	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	Palmitic acid	Palm oil
18	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	Stearic acid	Beef tallow
16	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	Palmitoleic acid	Butter
18	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	Oleic acid	Olive oil
18	$\text{CH}_3(\text{CH}_2)_6\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	Linoleic acid	Soybean oil
18	$\text{CH}_3\text{CH}_2(\text{CH}=\text{CHCH}_2)_3(\text{CH}_2)_6\text{COOH}$	Linolenic acid	Linseed oil

Figure 16.5 Carbon skeletal structures. (a) Tristearin, a typical saturated fat molecule. (b) Trillinolenin, a typical polyunsaturated oil molecule.



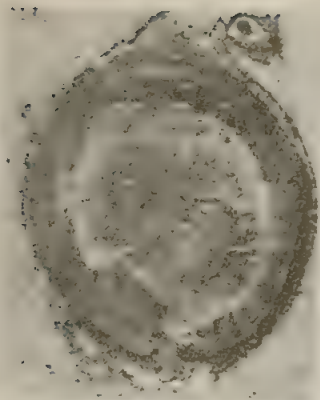


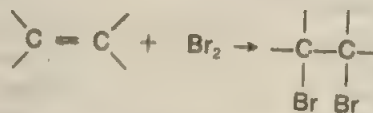
Figure 16.6 Photomicrograph of a cross section of a hardened artery, showing deposits of plaque. The deposits contain cholesterol. (Courtesy of Biomedical Graphics, University of Minnesota Hospitals, Minneapolis.)

The term *polyunsaturated*, often in the news and in advertisements during recent years, simply means that the molecules have fatty acid chains with two or more double bonds. Saturated fats have been implicated, along with cholesterol, as a factor in one type of arteriosclerosis, hardening of the arteries. Cause and effect have not been definitely proven, however.

Some grazing animals, such as cattle and sheep, have four-chambered stomachs. It is in the first of these chambers, the rumen, that unsaturated fatty acids from plants are hydrogenated to form animal fats. When young animals are suckling, the rumen is bypassed. Thus, researchers have been able to raise lambs to slaughtering age on a milk-based diet high in unsaturated fats. The meat from the lambs showed 10 times as much polyunsaturated fats as the meat from the control animals. The lamb chops were delicious as well as nutritious.

Researchers working in Australia fed steers with a diet supplemented with highly unsaturated safflower oil that had been treated with formaldehyde to prevent hydrogenation in the rumen. The beef so produced was also much higher in polyunsaturated fats. An understanding of the biochemical mechanism of hydrogenation may someday provide us with polyunsaturated lamb chops and beefsteaks, courtesy of a group of scientists willing to go "roamin' in the rumen."

The degree of unsaturation of a fat or an oil usually is measured by the *iodine number*. Chlorine and bromine add readily to carbon-carbon double bonds.



Iodine also adds, but less readily. The iodine number of a fat is the number of grams of iodine that will be consumed by 100 g of fat or oil. The more double bonds a fat contains, the more iodine required for the addition reaction; thus, a high iodine number means a high degree of unsaturation. Representative iodine numbers are listed in **table 16.2**. Notice the generally lower values for the animal fats (butter, tallow, lard) compared to those for the vegetable oils.

Table 16.2
Typical iodine numbers for some fats and oils

<i>Fat or Oil</i>	<i>Iodine Number</i>
Butter	25–40
Beef tallow	30–45
Lard	45–70
Olive oil	75–95
Peanut oil	85–100
Cottonseed oil	100–117
Corn oil	115–130
Fish oils	120–180
Soybean oil	125–140
Safflower oil	130–140
Sunflower oil	130–145
Linseed oil	170–205

Fats and oils feel greasy. They are insoluble in water but soluble in organic solvents such as carbon tetrachloride, gasoline, and ether. Fats and oils are lighter than water, and consequently they float on top of water when they are put into it.

When violently shaken together with water, fats are broken into tiny, sub-microscopic particles and dispersed through the water. Such a mixture is called an *emulsion*. Unless a third substance has been added, the emulsion breaks down rapidly. The droplets then recombine and float to the surface of the water. Soap, certain types of gum, or protein can stabilize the emulsion by forming protective coatings on the fat droplets that prevent them from coming together. Milk is an emulsion of butterfat in water. The stabilizing agent in milk is a protein called casein.

Fats are high-energy foods. They yield about 9 kcal of energy per gram. (If you were backpacking on a camping trip and wanted to get the maximum food energy per pound of food, you'd take along a pound of lard.) Some fats are "burned" as fuel for our activities. Others are used to build and maintain important constituents of our cells, such as the cells of brain and nerve tissue and the membranes that surround each cell.

Fats eaten in excess are stored in the body, where they serve as energy reserves. This stored fat also serves to insulate the body against loss of heat and to protect vital organs from injury by acting as extra padding.

Fat in our diet comes from butter, cream, oleomargarine, vegetable oils and shortenings, meat products, and some seeds and nuts. About 10% of our diet by weight should be fats. Few people in the United States have to worry about getting too little fat; a typical American's diet consists of 30% to 40% fat.

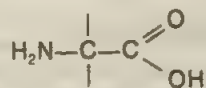
Proteins: The Stuff of Life

The third class of food, the proteins, is the vital component of all life. No living part of the human body—or of any other kind of animal, for that matter—is completely without protein. There is protein in the blood, the muscles, the brain, and even the tooth enamel. The smallest cellular organisms, the bacteria, contain protein. And the viruses, so small that they make the bacteria look like giants, are nothing but large molecules of a special type of protein. This special material, called *nucleoprotein*, is found in all cells and is the stuff of life itself. Nucleoproteins are combinations of proteins with nucleic acids. As we saw in chapter 11, these nucleic acids control the structure and function of cells. This they do through the proteins they cause to be formed.

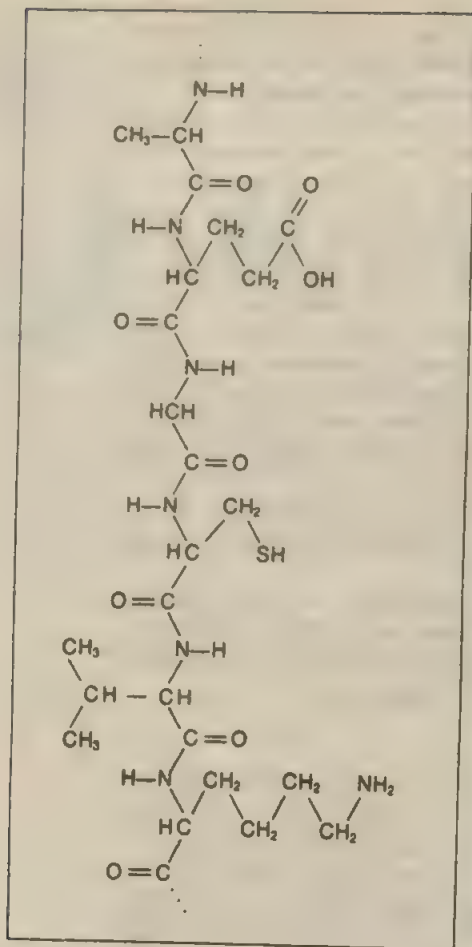
Each type of cell makes its own specific kinds of proteins. The proteins serve as the structural material of animals, much as cellulose does for plants. Muscle tissue is largely protein. So are skin and hair. These proteins are made in different forms in different animals. Silk, wool, nails, claws, feathers, horns, and hoofs are proteins.

All proteins contain the elements carbon, hydrogen, oxygen, and nitrogen. Most proteins also contain sulfur. The structure of a short segment of a typical protein molecule is shown in **figure 16.7**.

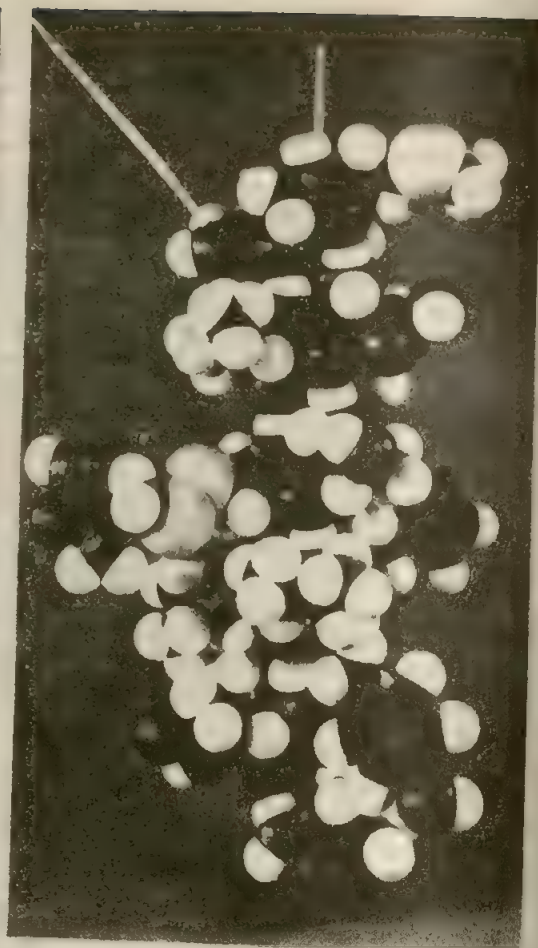
Proteins are copolymers of about 20 different *amino acids*. Amino acids have two functional groups. The amino group (—NH_2) is on the carbon next to that of the carboxyl group (—COOH).



This partial formula indicates the proper placement of these groups, but the structure is not really correct. Acids react with bases to form salts; the carboxyl group is acidic and the amino group is basic. Therefore, these two functional groups

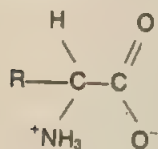


(a)



(b)

Figure 16.7 (a) Structural formula of a segment of a protein molecule. (b) A space-filling model of a segment of a protein chain. (Courtesy of Science Related Materials, Inc., Janesville, Wis)



An amino acid

interact, the acid transferring a proton to the base. The resulting product is an inner salt, or *zwitterion*, a compound in which the anion and the cation are parts of the same molecule. The amino acids differ in that a variety of other groups (symbolized by the —R) may be attached to the carbon atom that bears the amino group.

Plants are able to synthesize proteins from carbon dioxide, water, and minerals such as nitrates (NO_3^-) and sulfates (SO_4^{2-}). Animals, in their digestive tracts, break down proteins from plant matter or animal flesh into the component amino acids. From these, the animals can synthesize proteins for growth and for the repair of body tissues.

When a diet contains more protein than is needed for the body's growth and repair, the leftover protein can be used as a source of energy.

The Essential Amino Acids: Eat 'em or Else

The adult human body can synthesize all but eight of the amino acids needed for making proteins. Those eight (they are indicated in **figure 16.8**) are called *essential amino acids*. They must be included in our diet. We eat proteins, break them down in our bodies to their constituent amino acids, and then use some of these amino acids to build other protein structures essential for our health. Each of the essential amino

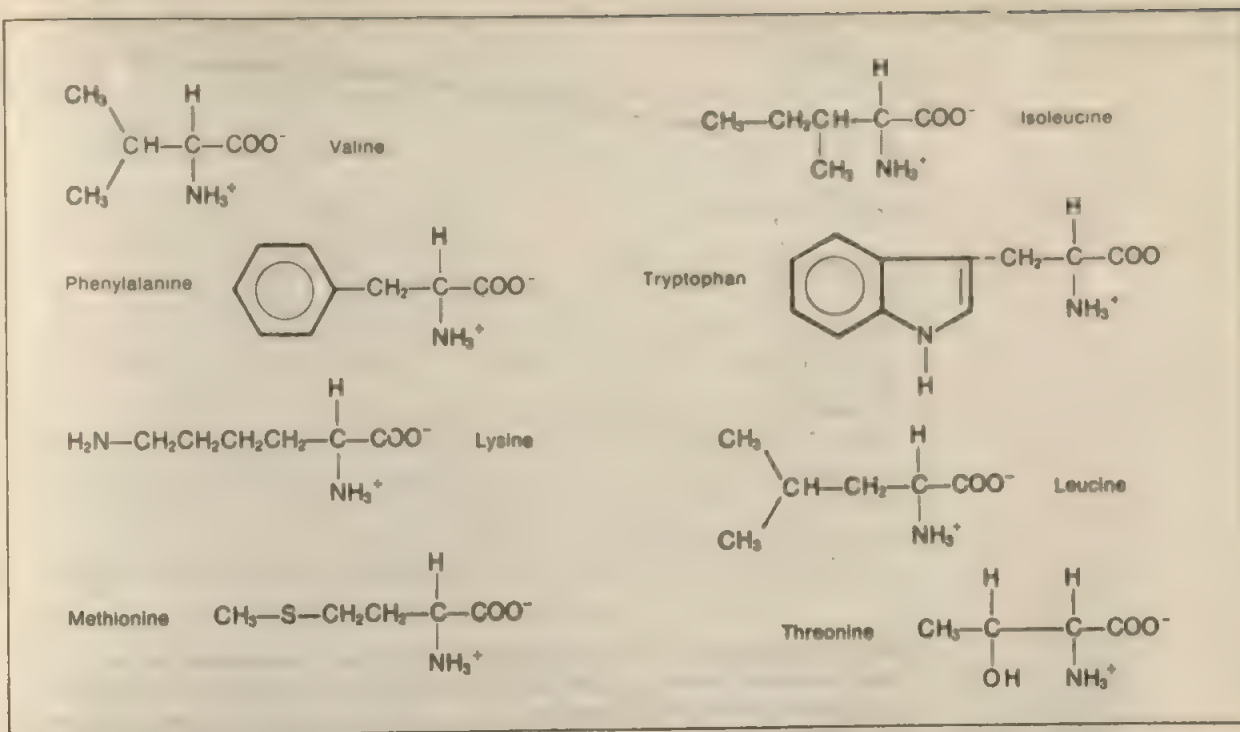


Figure 16.8 The eight amino acids essential to adult humans.

acids is a *limiting reagent*. When the body runs out of one of them, it can't make proper proteins.

An *adequate protein* supplies all the essential amino acids in the quantities needed for the growth and repair of body tissues. Most proteins from plant sources are deficient in one or more amino acids. Corn protein is lacking in lysine and tryptophan. People whose diet consists chiefly of corn may suffer from malnutrition even though the amount of calories supplied by the food is adequate. Protein from rice is short of lysine and threonine. Wheat protein is lacking in lysine. Even soy protein, probably the best nonanimal protein, is lacking in the essential amino acid methionine.

The breeding of high-lysine corn has met with some success. There is promise that other cereal grains can be bred to produce more and better proteins. Missing amino acids also can be supplied as additives to inadequate proteins. This technique has been used, for the most part, though, for enhancing the nutritional value of animal feeds.

Most proteins from animal sources contain all the essential amino acids in adequate amounts. Lean meat, milk, fish, eggs, and cheese supply adequate proteins. In fact, gelatin is about the only inadequate animal protein. It contains almost no tryptophan and has only small amounts of threonine, methionine, and isoleucine.

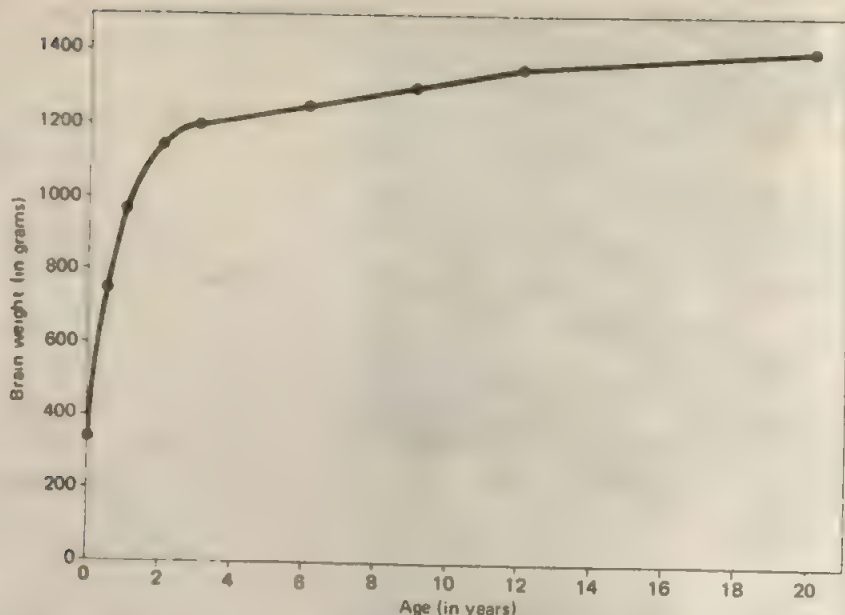
A proper diet should consist of about 20% protein by weight. It must include all the essential amino acids in sufficient quantity. Diets with inadequate protein are common in much of the world. A protein-deficiency disease called kwashiorkor (figure 16.9) is all too common in parts of Africa where corn is the major food. As populations increase, animal protein will become scarcer in the developed countries, too.

Nutrition is especially important in a child's early years. Protein deficiency leads



Figure 16.9 A lack of proteins and vitamins causes the deficiency disease known as kwashiorkor, which can be recognized by an affected individual's retarded growth, discoloration of skin and hair, bloating, swollen belly, and mental apathy. (Courtesy of Paul Almasy, World Health Organization.)

Figure 16.10 Growth of the human brain according to age

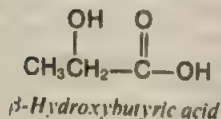
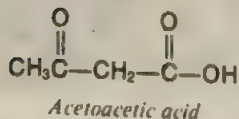
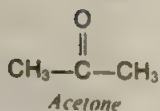


to both physical and mental retardation. The effect on a human's mental capacity is readily apparent from a consideration of **figure 16.10**, which shows that the human brain reaches nearly full size by the age of 2 years. Inadequate nutrition for a child in his or her mother's womb and at her breast may well hopelessly handicap the child for life.

Starvation, Fasting, and Fad Diets

When the human body is totally deprived of food, whether voluntarily or involuntarily, the condition is known as *starvation*. During total fasting, the body's glycogen stores are depleted rapidly and the body calls on its fat reserves. Fat is first taken from around the kidneys and the heart. Then it is removed from other parts of the body. Ultimately, even the bone marrow (which is also a fat-storage depot) is depleted, and it becomes red and jellylike (it is usually white and firm).

Increased dependence on fats as an energy source leads to *ketosis*, a condition characterized by the appearance of *ketones* in the urine. One of the ketones is acetone (chapter 11). Two other compounds are also prominent in the urine during ketosis: acetoacetic acid and β -hydroxybutyric acid. Collectively, these three compounds are called *ketone bodies* (even though one is not a ketone). Note that two of the ketone bodies are acids. Ketosis rapidly develops into *acidosis*; the blood pH drops and oxygen transport is hindered. Oxygen deprivation leads to depression and lethargy. Even the ability to think clearly and the ability to make decisions are impaired.



In the more extreme low-carbohydrate diets (for weight loss), ketosis is deliberately induced. Understandably, two of the side effects of these diets are often depression and lethargy. In the early stages of a diet deficient in carbohydrates, the body converts amino acids to glucose. The brain must have glucose; it can't obtain sufficient energy from fats. If there are enough adequate proteins in the diet, tissue proteins are spared. (The liquid protein diets, from which several people died, were based on the inadequate proteins obtained from beef hides and connective tissues.)

In the early stages of a *total fast*, body protein is metabolized at a relatively rapid rate. After several weeks, the rate of protein breakdown slows considerably as the

brain adjusts to using the breakdown products of fatty acid metabolism for its energy source. When fat reserves are substantially depleted, the body must again draw heavily on its structural proteins for its energy requirements. The emaciated appearance of a starving individual is due to the depletion of muscle proteins.

Even those low-carbohydrate diets that are high in adequate proteins are hard on the body, which must rid itself of the nitrogen compounds—ammonia (NH_3) and urea—formed by the breakdown of proteins. This puts an increased stress on the liver, where the waste products are formed.

It is interesting to note that, contrary to a popular notion, fasting does not cleanse the body. Indeed, quite the reverse occurs. A shift to fat metabolism produces the ketone bodies and protein breakdown produces ammonia, urea, and other wastes. You can lose weight by fasting, but the process should be carefully monitored by a physician.

Involuntary starvation is a serious problem in much of the world. Even so, starvation is seldom the sole cause of death. Weakened by starvation, the victims of starvation and malnutrition succumb to disease. Even minor diseases such as chicken pox and measles become life-threatening disorders. Barring disease, starvation alone would lead eventually to death from circulatory failure when the heart muscle became too weak to pump blood.

Thermodynamics, Vegetarians, and Ethnic Dishes

Green plants such as grasses and grains trap a small fraction of the energy of the sun that falls upon them. They use this energy to convert carbon dioxide, water, and mineral nutrients (including nitrates, phosphates, and sulfates) into proteins. Cattle eat the plant protein, digest it, and convert a small portion of it into animal protein. People eat this animal protein, digest it, and reassemble some of the amino acids into human protein. Some of the energy originally trapped by the green plants is lost as heat at every step of the food chain (see table 16.3). If people ate the plant protein directly, one highly inefficient step could be skipped. Vegetarianism is in harmony with the conservation of energy.

Table 16.3
Efficiencies of protein conversions*

Food	Efficiency of Production (%)
Beef or veal	4.7
Pork	12.1
Chicken or turkey	18.2
Milk	22.7
Eggs	23.3

Data from President's Science Advisory Committee, *The World Food Problem*, vol. 2, 1967.

*The efficiencies are calculated by dividing the weight of edible protein by the weight of the protein feed required to produce it and then multiplying the result by 100 to give a percentage.

It is interesting to note that a variety of ethnic dishes supply relatively good quality protein by combining a cereal grain with a legume (beans, peas, peanuts, etc.). The grain is deficient in tryptophan and lysine, but it has sufficient methionine. The legume is deficient in methionine, but it has enough tryptophan and lysine. A list of a few such combinations is provided in table 16.4. It should be noted, however, that the grain must be a whole grain. There is little protein of any kind in refined white flour and polished rice.

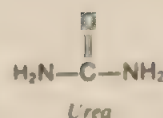


Table 16.4
Ethnic foods that provide relatively good proteins
by combining a cereal grain with a legume

<i>Ethnic Group</i>	<i>Food</i>
Mexican peasants	Corn tortillas and refried beans
Japanese	Rice and soybean curds (Tofu)
English working classes	Baked beans on toast
American Indians	Corn and beans (succotash)
Children (especially in the United States)	Peanut butter sandwiches
Western Africans	Rice and peanuts (ground nuts)
Cajuns (Louisiana)	Red beans and rice

Although complete proteins can be obtained by a careful mixture of vegetable foods, extreme vegetarianism is dangerous. Even when the diet includes a wide variety of plant materials, an all-vegetable diet is likely to lack vitamin B₁₂ because this nutrient is not found in plants. Other nutrients scarce in all-plant diets include calcium, iron, riboflavin, and (for children not exposed to sunlight) vitamin D. A modified vegetarian diet that includes milk, eggs, cheese, and fish can provide excellent nutrition, with red meat totally excluded.

Stretching Exercises: Meat Analogs and Extenders

Meat is often scarce and always expensive, even in the developed countries. Consequently, a variety of supplements and substitutes have been developed. Budget-conscious cooks have long used bread crumbs, oatmeal, dried milk, and other products to stretch ground-meat dishes. But, with the exception of dried whole milk, these extenders are deficient in protein.

A good deal of research has gone into the development of meat analogs from soy protein. The protein is extracted from soybean meal and spun into fibers (**figure 16.11**). These fibers then are treated with flavorings and other additives and formed to resemble bits of bacon, ground beef, or even chicken or ham. With the exception of "bacon" bits, these products have not been widely accepted for home cooking. However, they have become widely popular on the institutional food market and are used mostly to extend ground-meat products. Mixtures of meat containing up to 25% soy protein provide essentially the same nutrition as pure meat and are somewhat cheaper. One drawback that has been reported is that the soy protein seems to retain some of the fat that would ordinarily cook out of the meat.

Minerals: Important Inorganic Chemicals in Our Lives

As might be expected, many of the chemicals in living organisms are organic. But there are also inorganic chemicals that are vital to sustaining life. These inorganic nutrients are called *minerals*. It is estimated that minerals represent about 4% of the weight of a human body. Some of these, such as the chlorides (Cl⁻), phosphates (PO₄³⁻), bicarbonates (HCO₃⁻), and sulfates (SO₄²⁻), occur in the blood and the other body fluids. Others, such as iron (as Fe²⁺) in the hemoglobin and phosphorus in the nucleic acids (DNA and RNA), are constituents of very complex organic compounds.

Minerals essential to one or more living organisms include the elements sodium (Na), magnesium (Mg), potassium (K), phosphorus (P), sulfur (S), chlorine (Cl),

Figure 16.11 Part of the manufacturing process in the General Mills vegetable-protein-foods plant at Cedar Rapids, Iowa, resembles that for spinning rayon or nylon. In this photograph, liquid protein has been fed into a spinning machine and emerges as bands of thin, white fibers. To these bands of vegetable protein fibers, color and flavor are eventually added. Then they are cut into various shapes and sizes, packaged, and sold under the company's BONTRAE[®] label to the institutional food market or as Bac[®]Os and other consumer products. (Courtesy of General Mills, Inc. Minneapolis.)

calcium (Ca), manganese (Mn), iron (Fe), copper (Cu), cobalt (Co), zinc (Zn), iodine (I), fluorine (F), silicon (Si), tin (Sn), vanadium (V), chromium (Cr), selenium (Se), molybdenum (Mo), and arsenic (As). Together with the structural elements carbon, hydrogen, nitrogen, and oxygen, these make up the 28 chemical elements essential to life. Other elements are sometimes found in body fluids and tissues but are not known to be essential. These include aluminum (Al), lithium (Li), nickel (Ni), and boron (B). Eventually, it may be discovered that one or more of these is essential, also.

These minerals serve a variety of functions. The function of iodine is perhaps the most dramatic. A small amount of iodine is necessary for the thyroid gland to function properly. A deficiency of iodine has dire effects, of which goiter is perhaps the best known. Iodine is available naturally in seafood. But, to guard against iodine deficiency, a small amount of sodium iodide (NaI) is added to table salt (NaCl). The use of iodized salt has greatly reduced the incidence of goiter.

Iron(II) ions (Fe^{++}) are necessary for the proper function of the oxygen-transporting compound hemoglobin. Without sufficient iron, not enough oxygen is supplied to the body tissues. Anemia, a general weakening of the body, results. Foods especially rich in iron compounds include red meat and liver.

Calcium and phosphorus are necessary for the proper development of bones and teeth. Growing children need about 1.5 g of each per day. Plenty of these elements are available from milk. The needs of adults for these elements are less widely known but are very real just the same. For example, calcium ions are necessary for the coagulation of blood (to stop bleeding) and for maintenance of the rhythm of the heartbeat. Phosphorus is necessary in order for the body to obtain energy from carbohydrates. Without phosphorus compounds, we couldn't get *any* energy from those quick-energy foods. Compounds containing phosphorus also play many other essential roles in the functioning of the body.

Sodium chloride in moderate amounts is essential to life. It is important in the exchange of fluids between cells and plasma, for example. The presence of salt increases water retention. A high volume of retained fluids can cause swelling and high blood pressure (hypertension). There are an estimated 23 million people in the United States who suffer from hypertension. And most physicians agree that our diets generally contain too much salt.

Iron, copper, zinc, cobalt, manganese, molybdenum, calcium, and magnesium are essential to the proper functioning of metallo-enzymes, which are life sustaining. The functions of some of the other minerals are quite complex. Something of how they operate is known, but a great deal remains to be learned about the role of inorganic chemicals in our bodies. Bioinorganic chemistry is a flourishing area of research.

The Vitamins: Vital, but Not All Are Amines

Why are British sailors called "limeys"? And what does that have to do with food? Sailors have been plagued since early times by *scurvy*. In 1747, a British navy captain showed that the disease could be prevented by the inclusion of fresh fruit and vegetables in the diet. A convenient fresh fruit to carry on long voyages (they didn't have refrigeration) was the lime. British ships put to sea with barrels of limes aboard, and the sailors ate a lime or two every day. That is how they came to be known as "lime eaters" or simply "limeys."

In 1897, the Dutch scientist Christiaan Eijkman showed that polished rice lacked something found in the hulls. Lack of that something caused the disease *beriberi*, which was quite a problem in the Dutch East Indies at that time.

A British scientist, F. G. Hopkins, fed a synthetic diet of carbohydrates, fats,

proteins, and minerals to a group of rats. The rats were unable to sustain healthy growth. Again, something was missing.

In 1912, Casimir Funk, a Polish biochemist, coined the word *vitamine* (from the Latin word *vita*, meaning life) for these missing factors. Funk thought that all factors contained the amino group. In the United States, the final *e* was dropped after it was found that not all the factors were amines. The generic term became *vitamin*. Eijkman and Hopkins shared the 1929 Nobel Prize in medicine and physiology for their important discoveries.

Vitamins are specific organic compounds, unrelated chemically, which are required in the diet (in addition to the usual proteins, fats, carbohydrates, and minerals) to prevent specific diseases. Some of the vitamins, their structures, sources, and deficiency symptoms are given in **table 16.5**. The role of vitamins in the prevention of deficiency diseases has been well established. In recent years, massive doses of vitamins have been recommended as preventives or cures for diseases as varied as the common cold and schizophrenia. We discuss this sort of megavitamin therapy in chapter 22.

Table 16.5
Some of the vitamins

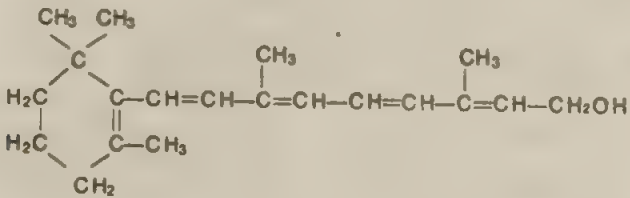
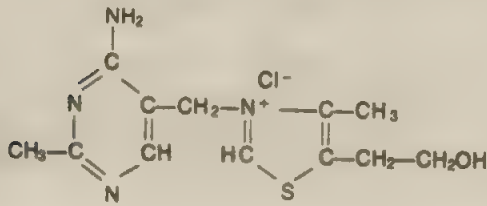
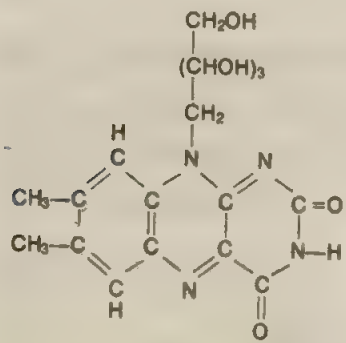
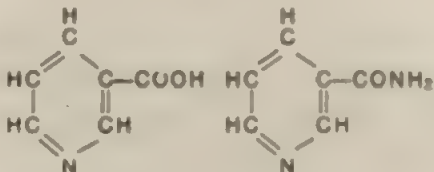
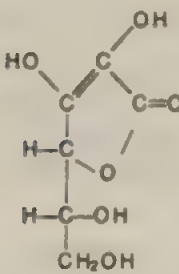
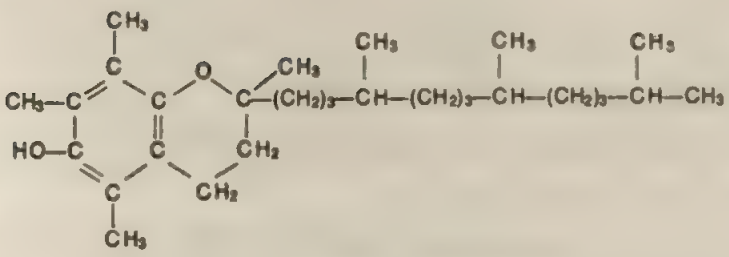
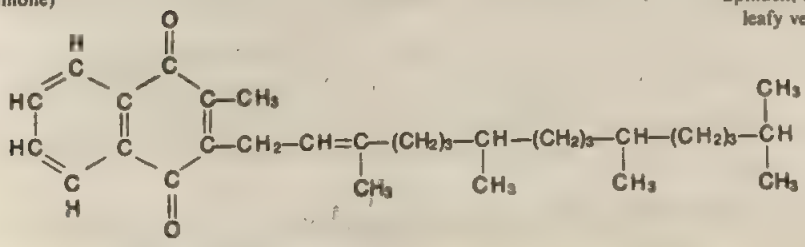
Vitamin	Structure	Good Source	Deficiency Symptom
A		Fish, liver, eggs, butter, cheese; also a vitamin precursor in carrots and other vegetables	Night blindness
B ₁ (thiamine)		Germ of cereal grains, legumes, nuts, milk	Beriberi
B ₂ (riboflavin)		Milk, red meat, liver, egg whites, green vegetables, fish	Dermatitis, glossitis

Table 16.5 continued

Vitamin	Structure	Source	Deficiency Symptom
Niacin (nicotinic acid and nicotinamide)		Red meat, liver, coffee (niacin is another of the B complex vitamins)	Pellagra
B ₁₂	(for structure, see reference 7, p. 554)	Liver, meat, eggs, fish	Pernicious anemia
C (ascorbic acid)		Citrus fruits, tomatoes, green peppers	Scurvy
D	(for structure, see p. 143)	Cod liver oil, irradiated ergosterol (milk supplement)	Rickets
E		Wheat germ oil, green vegetables, egg yolks, meat	Sterility, muscular dystrophy
K ₁ (phylloquinone)		Spinach, other green leafy vegetables	Hemorrhage

Fiber: A Nonfood with an Important Function

The importance of fiber, or roughage, in the diet often was ignored or overlooked until the mid-1970s. Then, some studies were published that got the public excited about fiber. First, it was noted that people in the developed countries are much more likely to get cancer of the colon than are those in the underdeveloped nations. Also, people in the developed countries eat diets rich in highly processed, low-bulk foods, while those in more "primitive" areas eat high-fiber diets. High-fiber diets lead to frequent and robust bowel movements. In addition to providing bulk, the fiber absorbs a lot of water, leading to softer stools. Low-bulk diets result in less frequent bowel action, with high retention times for feces in the colon.

Bacteria act upon the materials in the colon. (Indeed, bacteria, both living and dead, make up about 33% of the dry weight of feces.) With a high-fiber diet, the materials seldom remain in the colon for more than a day. With a low-bulk diet, the retention time can be as long as 3 days, thus allowing for prolonged bacterial activity that produces a high level of mutagenic chemicals. Chemicals that are mutagenic often are also carcinogenic. Thus, a possible chemical link between low-fiber diets and cancer of the colon has been established.

Cellulose makes up the greater part of dietary fiber. It comes only from plant sources. The fibrous portions of plants (stems, peels, and seeds) are rich in fiber. Wheat bran, celery, green beans, apple peels, and fruits eaten with seeds (such as raspberries, strawberries, and figs) are excellent sources of dietary fiber.

Processed Food: Less Nutrition?

Whole wheat is an excellent source of vitamin B₁ and other vitamins. To make white flour, the wheat germ and bran are removed from the grain. The remaining material is almost pure starch. It has little protein, few minerals, and no vitamins. We eat the starch and use the germ and bran for animal food. At least our cattle and hogs get good nutrition.

Similarly, polished rice has had most of its protein and minerals removed, and it has virtually no vitamins. The disease beriberi, mentioned before, became prevalent when polished rice was introduced into Southeast Asia.

When fruits and vegetables are peeled, most of their vitamins, minerals, and fibers are lost. The peels may be dumped (directly or through a garbage disposal) into a nearby stream, where they contribute to water pollution (chapter 18). The heat used to cook food also destroys some vitamins. If water is used in cooking, part of the water-soluble vitamins (C and B complex) and some of the minerals often are drained off and discarded with the water.

The methods that we use for processing and cooking food often are chosen for aesthetic reasons, but sometimes cooking methods help preserve the food. For example, highly milled flour does keep better than whole wheat flour. Cooked tomatoes keep better than fresh tomatoes, although their vitamin C is partly destroyed by cooking. But tomatoes, potatoes, and apples are peeled merely because they look better that way.

It is estimated that over 50% of the diet of the average person in the United States consists of processed foods. The "teenager's" diet of hamburgers, potato chips, and colas is lacking in many essential nutrients. Highly processed convenience foods threaten to leave the people of our nation, with its abundance of food, rather poorly nourished.

Energy Is Conserved: Calories Do Count

There are hundreds of books and perhaps thousands of products on the market

that promise the overweight a quick and easy way to get rid of those extra pounds. In reality, there are only two ways to lose weight, and only one of those is safe.

To understand the safe way of weight loss, remember the first law of thermodynamics: energy is conserved. If you take in less in food calories than you use up, your body will obtain energy from stored fat and you will lose weight. Of course, the opposite is also true. More about that in a moment.

The other way to lose weight is to induce deliberately a pathological condition. A simple method, which one fellow sold quite profitably for a while, is to ingest tapeworm eggs. A part of your food energy then is diverted to the growth of the parasite, and weight is lost as the segmented worm drops off egg-laden sections. Another method, more common and much more profitable, is one variant or another of the low-carbohydrate diet (p. 224). These diets work by shifting the metabolism to a less efficient process. Keep in mind, though, that the weight loss may be mainly muscle, not fat.

Now back to the safe way to lose weight. A simple way is to keep your activity level the same and reduce your food intake. Say, for example, that you normally burn up 2500 kcal per day. When you go on a reducing diet and take in 1500 kcal per day, you will burn off 1000 kcal of fat per day. There are 454 g of fat in 1 lb and 9 kcal in 1 g of fat. That means there are 4086 kcal per pound of fat. Burning off 1000 kcal per day, you would lose a pound of fat in 4 days. That is about the maximum safe rate for weight loss. If the diet were continued, you would lose about 8 lb per month and 96 lb in a year.

Let's consider doing it the other way: keep your food intake constant and increase your activity. Be forewarned, however, that weight loss through exercise is a slow process. Say you take up jogging. You work at it until you can do a mile in 8 minutes. You will burn off about 155 kcal per mile. To burn off a pound of fat (4086 kcal), you have to run 26.3 mi. That's the marathon distance! (You may experience a much more substantial weight loss during physical activity, but that loss is largely fluid lost through perspiration.) Exercise will bring about weight loss when continued on a routine basis several times a week. Of course, exercise is also beneficial in many other ways.

How do we get all that weight on in the first place? It's easy. Munch a few potato chips while watching television. Say you eat five chips a day beyond your normal food intake. Those five potato chips have 50 kcal of energy. In 82 days, you will have gained a pound of fat. That's 4.5 lb a year. Or, maybe, you drink one 7-oz glass of

Table 16.6
Activities and energy consumption*

Activity	Kilocalories Burned Off per Hour
Watching television	70
Normal conversation	110
Driving an automobile	170
Walking	300
Bicycling	480
Swimming	650
Running	1100

*Values given are in kilocalories and are approximate for an individual who weighs about 140 lbs. Activities are assumed to be at a moderate rate.

beer above your normal food intake. That's 114 kcal. You'll gain a pound in 36 days. That's 10 lbs a year!

Not everybody likes jogging, beer, or potato chips. **Table 16.6** provides a list of activities and the calories consumed by engaging in the activities. Similarly, **table 16.7** provides a list of foods and their caloric values. From these you may be able to calculate what your favorite activity or food does for you in taking off those pounds or in putting them on.

Table 16.7
Typical energy content of several foods

<i>Food</i>	<i>Serving</i>	<i>Kilocalories</i>
Apple	1 large	100
Apple pie	1/6	380
Banana	1 small	65
Beer	12 oz	165
Cabbage, raw	1 cup	25
Candy, chocolate	1 oz	145
Cantaloupe	1/2 medium	40
Egg, boiled	1 medium	80
Hamburger, doubledecker	1 giant	1200
Hamburger, plain	1 medium	350
Milk, skim	8 oz	90
Milk, whole	8 oz	160
Milkshake	1 pt	500
Peanuts, roasted	1/2 cup	400
Pizza, cheese	1/8 medium	180
Pop	12 oz	145
Potato, baked	1 medium	95
Potato, french fried	1 medium	160
Potato chips	10 medium	110
Yogurt, whole milk, unsweetened	1 cup	170

Problems

- List the three major types of food. What is the role of each in the human diet?
- What is the role of each of the following in the human diet?
a. vitamins b. minerals c. fibers
- In general, what are the problems associated with a strict vegetarian diet?
- Explain why a diet high in meat products makes less efficient use of the energy originally captured by plants through photosynthesis.
- How does a fat differ from an oil in physical properties? In structure?
- Which would you expect to have a higher iodine number, peanut oil or beef tallow? Explain your reasoning.
- Which would you expect to have a high iodine number, hard or liquid margarine? Explain your reasoning.
- List four vitamins. Give a good food source for each. List the deficiency symptom for each.
- How long would you have to walk to burn off the 1200 kcal in one giant doubledecker hamburger if your walking used 300 kcal per hour?
- How long would you have to run to burn off the 110 kcal in 10 potato chips if your running burns off 1100 kcal per hour?
- If you used up 100 kcal per day more than you take in, how long would it take you to lose 1 lb of fat? (There are about 4000 kcal in 1 lb of fat.)

12. What are essential amino acids? What is their role in nutrition?
13. Which essential amino acid(s) are likely to be lacking in corn? In beans?
14. A new bread is made by adding pea flour to wheat flour. Would the bread provide adequate protein? Why or why not?
15. How far would you have to run to burn off 10 lb of fat if your running (at a pace of 8 minutes per mile) burns off 155 kcal per mile? (Assume that there are 4000 kcal in 1 lb of fat.)
16. Graham crackers are 11% protein. Assume that your Recommended Daily Allowance (RDA) is 60 g of protein. What percentage of your RDA of protein would you receive if you ate 150 g of graham crackers?
17. Assume that 1 cup of skim milk contains 22 g. Skim milk is 1.6% protein. How much protein is there in 4 cups (1 qt) of skim milk?

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chapter 17

Food Additives: Bane or Blessing?

The label reads egg whites, vegetable oils, nonfat dry milk, lecithin, mono- and diglycerides, propylene glycol monostearate, xanthan gums, sodium citrate, aluminum sulfate, artificial flavor, iron phosphate, niacin, riboflavin, and irradiated ergosterol. You read it and find only a few of the ingredients recognizable. You still want to know what's in the package. Most of the substances listed are *food additives*: substances other than basic foodstuffs that are present in food as a result of some aspect of production, processing, packaging, or storage.

There are two broad types of food additives. *Intentional additives* are those put in a product on purpose to perform a specific function. *Incidental additives* are those that get in accidentally during production, processing, packaging, or storage. Pesticide residues, insect parts, and antibiotics added to animal feeds are examples of the incidental additives that sometimes get into our food.

In this chapter, we consider mainly the intentional additives and how these chemicals affect our enjoyment of food, our health, and our well-being.

Why Food Additives?

We said in chapter 16 that processing results in the removal or destruction of certain essential food substances. Therefore, in some cases, it is necessary to add additives to the prepared food in order to increase its nutritional value. Other chemicals are added to enhance color and flavor, to retard spoilage, to provide texture, to sanitize, to bleach, to ripen (or to prevent ripening), to control moisture or dryness, to prevent (or enhance) foaming, and to perform a variety of other functions.

In the United States, food additives are regulated by the Food and Drug Administration. The original Food, Drug, and Cosmetic Act was passed by Congress in 1938. Under that act, the Food and Drug Administration had to prove that an additive was unsafe before it could prevent its use. The Food Additives Amendment of 1958 shifted the burden of proof to the industry. A company wishing to use a food additive must first furnish proof to the FDA that the additive is safe for its intended use. The amount of chemical that can be added is regulated, also.

Table 17.1
Your breakfast—as seen by a chemist*

Chilled Melon:

Starches	Anisyl propionate
Sugars	Amyl acetate
Cellulose	Ascorbic acid
Pectin	Vitamin A
Malic acid	Riboflavin
Citric acid	Thiamine
Succinic acid	

Scrambled Eggs:

Ovalbumin	Lecithin
Conalbumin	Lipids (fats)
Ovomucoid	Fatty acids
Mucin	Butyric acid
Globulins	Acetic acid
Amino acids	Sodium chloride
Lipovitellin	Lutein
Livetin	Zeaxanthine
Cholesterol	Vitamin A

Sugar-Cured Ham:

Actomyosin	Adenosine tri-phosphate (ATP)
Myogen	Glucose
Nucleoproteins	Collagen
Peptids	Elastin
Amino acids	Creatine
Myoglobin	Pyroligneous acid
Lipids (fats)	Sodium chloride
Linoleic acid	Sodium nitrate
Oleic acid	Sodium nitrite
Lecithin	Sodium phosphate
Cholesterol	
Sucrose	

Coffee:

Caffeine	Acetone
Essential oils	Methyl acetate
Methanol	Furan
Acetaldehyde	Diacetyl
Methyl formate	Butanol
Ethanol	Methylfuran
Dimethyl sulfide	Isoprene
Propionaldehyde	Methylbutanol

Cinnamon Apple Chips:

Pectin	Propanol
Cellulose	Butanol
Starches	Pentanol
Sucrose	Hexanol
Glucose	Acetaldehyde
Fructose	Propionaldehyde
Malic acid	Acetone
Lactic acid	Methyl formate
Citric acid	Ethyl formate
Succinic acid	Ethyl acetate
Ascorbic acid	Butyl acetate
Cinnamyl alcohol	Butyl propionate
Cinnamic aldehyde	Amyl acetate
Ethanol	

Toast and Coffee Cake:

Gluten	Methyl ethyl ketone
Amylose	Niacin
Amino acids	Pantothenic acid
Starches	Vitamin D
Dextrins	Acetic acid
Sucrose	Propionic acid
Pentosans	Butyric acid
Hexosans	Valeric acid
Triglycerides	Caproic acid
Sodium chloride	Acetone
Phosphates	Diacetyl
Calcium	Maltol
Iron	Ethyl acetate
Thiamine	Ethyl lactate
Riboflavin	
Mono- and Diglycerides	

Tea:

Caffeine	Phenyl ethyl alcohol
Tannin	Benzyl alcohol
Essential oils	Geraniol
Butyl alcohol	Hexyl alcohol
Isoamyl alcohol	

[From Manufacturing Chemists Association, Washington, D.C.]

*The chemicals listed are those that are found normally in the foods. No food additives are itemized. Also, please note that the chemical listings are not necessarily complete.

Food additives are not a recent development. Salt has been used to preserve meat and fish since the times people lived in caves. Spices have been used since earliest recorded history to flavor and preserve foods. Other additives have been used throughout the centuries. The movement of the population from farms to cities in recent years has increased the necessity of using additives to preserve foods. An increased desire for convenience foods also has led to greater use of additives. Competition for sales has caused industries to use more additives that make their food products more tasty and more attractive. These and other factors have led to a per capita consumption of about 4 kg per year of food additives in the United States.

Our increased consumption and our worry over problems caused by some food additives have led to a lot of anguish over food additives. This worry often is expressed as concern about "chemicals in our food." As we said in chapter 16, though, food itself is chemical. Table 17.1 shows the chemical composition of a typical breakfast. Many of the chemicals in the breakfast would be harmful in large amounts but are harmless in the trace amounts that occur naturally in foods. Indeed, some make important contributions to the flavors and aromas that make food so delightful.

Our bodies are also collections of chemicals. Broken down to its elements (table 17.2), your body would be worth about \$6.00 as chemicals. It is the unique combination of the elements in every human body, though, that makes you different from everyone else and makes each individual's value beyond measure. Since food is chemical and we are chemical, we shouldn't have to worry, in general, about chemicals in our food. Perhaps we should be concerned, however, about some of the chemicals in our food. Most of all, we should try to evaluate the potential hazards of food additives that are used now and may be used in the future—and the hazards of some chemicals that occur naturally in some foods.

Table 17.2
Approximate elemental analysis of the human body

<i>Element</i>	<i>Percentage (by Weight)</i>
Oxygen	65
Carbon	18
Hydrogen	10
Nitrogen	3
Calcium	1.5
Phosphorus	1
Potassium	0.35
Sulfur	0.25
Chlorine	0.15
Sodium	0.15
Magnesium	0.05
Iron	0.004
Total	100

Additives That Improve Nutrition

Only a small amount of iodine is necessary for the proper functioning of the thyroid gland. Iodine is plentiful in seafood, but people in inland areas often suffer

from iodine deficiency. A particularly striking result is goiter, a swelling of the thyroid often symptomized by an unsightly swollen neck. The first nutrient supplement approved by the Food and Drug Administration, potassium iodide (KI), was added to table salt in 1924 to reduce the incidence of goiter.

A number of other chemical additives have been added to foods specifically to prevent deficiency diseases. Nutrient supplements are still important today. The addition of vitamin B₁ (thiamine) to polished rice is essential in the Far East, where beriberi still is a problem.

The replacement of the B-complex vitamins thiamine, riboflavin, and niacin (which are removed in processing) and the addition of iron (usually ferrous carbonate, FeCO₃) to flour is called *enriching*. Enriched bread made from this flour still isn't as good a food as bread made from whole wheat. It lacks vitamin B₆, pantothenic acid, folic acid, and the minerals zinc and magnesium, nutrients usually provided by whole grain flour. An investigator in Texas fed enriched white bread to rats. Most of them died of malnutrition in fewer than 60 days. The staff of life, in its modern form, is unable to sustain life. However, the enrichment of bread, corn meal, and cereals has served to virtually eliminate pellagra, which once plagued the southern states of the United States (figure 17.1). Recognizing the potential danger of the large amounts of junk food in our diets, the Food and Drug Administration has moved to require the further enrichment of bread, cake, and other processed baked goods with iron, thiamine, riboflavin, and niacin.

Vitamin C (ascorbic acid) is added frequently to fruit juices, flavored drinks, and beverages. Although our diets generally contain enough ascorbic acid to prevent scurvy, a number of scientists recommend a much larger intake than basic minimum requirements. We discuss the use of massive dosages of C and other vitamins in chapter 22.

Vitamin D is added to milk used in the developed countries. This use of fortified milk has led to the virtual elimination of rickets. Similarly, vitamin A is added to margarine. (This vitamin occurs naturally in butter; it is added to margarine so that the substitute more nearly matches the nutritional quality of butter.)

If we ate a balanced diet of foods fresh from the farm, we probably wouldn't need nutritional supplements. With our usual diets rich in highly processed foods, however, we need the nutrients provided by vitamin and mineral food additives.

Molecular Flavors: Chemicals That Taste Good

If you like spice cake, soda pop, gingerbread, and sausage, you like food additives. These and many other foods depend for their flavor almost totally on spices and other flavorings. Cloves, ginger, cinnamon, and oregano are examples of natural spices. Natural flavors also can be extracted from fruits and other plant materials. Vanilla extract is a familiar example.

Chemists sometimes analyze a natural flavor and determine its components. Then, they synthesize the components and make a mixture that may closely resemble the natural product. The major components of natural and artificial flavors are often identical. For example, both vanilla extract and imitation vanilla flavoring owe their flavor mainly to vanillin (figure 17.2). The natural flavor is usually a good deal more complex than the imitation because the natural product contains a wider variety of chemicals than does the imitation. Indeed, some scientists say that the imitation, if anything, is safer than the natural flavoring because it contains fewer chemicals, and the chemicals that are in the imitation flavoring are identical to those in the natural product.

Flavors, whether natural or synthetic, probably present little hazard when they are used in moderation. And they contribute considerably to our enjoyment of food.



Figure 17.1 A severe case of acute pellagra. Niacin is called the anti-pellagra vitamin since its deficiency in human beings appears to be the chief cause of the disease. (Courtesy of the World Health Organization.)

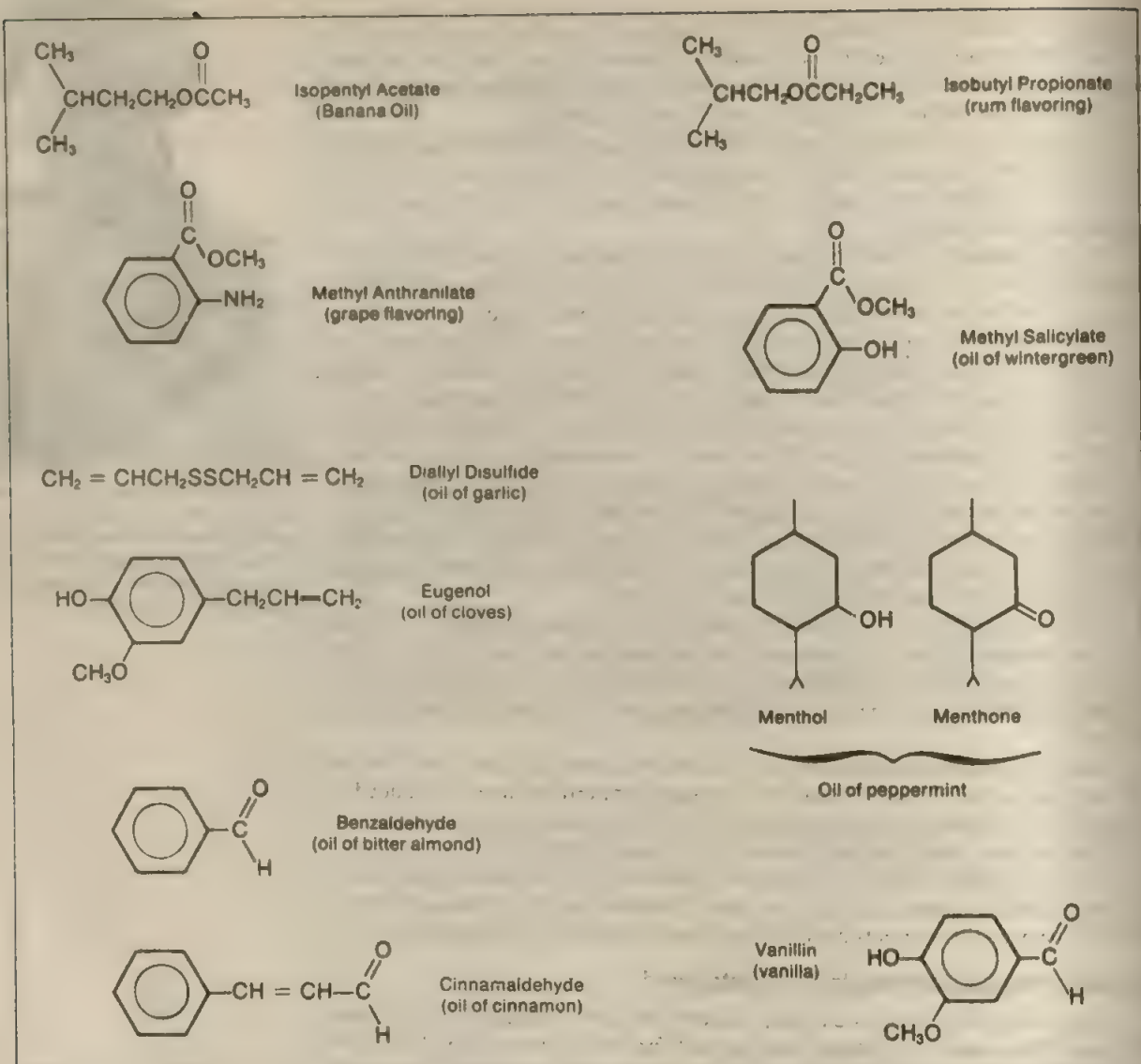


Figure 17.2 Some molecular flavorings

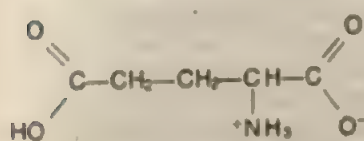
Additives That Enhance Flavors

Some chemical substances, though not particularly flavorful themselves, are used to enhance other flavors. Common table salt (sodium chloride, NaCl) is a familiar example. Salt seems to increase sweetness but helps to mask bitterness and sourness.

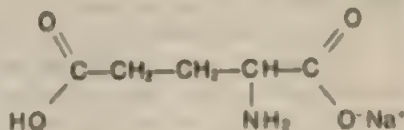
Salt is a necessary nutrient in moderate amounts. Many physicians and scientists contend that the average person's diet in the United States contains too much salt. Snack foods (crackers, potato chips, pretzels, etc.) are particularly heavy in salt. There is evidence that too much salt contributes to high blood pressure (hypertension).

Another popular flavor enhancer is monosodium glutamate (MSG). Glutamic acid is one of about 20 amino acids that occur naturally in proteins. MSG is the

sodium salt of glutamic acid. It is used in many convenience foods. It is also used heavily in many Chinese foods. Although glutamates are found naturally in protein, there is evidence that excessive amounts are harmful. A peculiar disease that long baffled physicians finally was traced to the regular consumption of Chinese foods. Certain individuals who seem particularly susceptible to MSG develop headaches and feel weak after eating in Chinese restaurants. The condition became known as the Chinese restaurant syndrome.



Glutamic Acid



MSG

Those individuals who are susceptible to Chinese restaurant syndrome may find it difficult to avoid MSG. MSG often is an ingredient of foods for which the Food and Drug Administration has established *standards of identity*. Such foods must contain certain ingredients in certain proportions. They may, however, contain certain other substances, as well. Mayonnaise and salad dressing are examples of standard foods. Standard foods may contain MSG even when it is not included in the list of ingredients on the labels.

For many years, MSG was added to baby foods. This was done, presumably, to please the parents because babies do not have a highly developed sense of taste and wouldn't have known the difference. Public pressure, coming after MSG was found to numb portions of the brains of laboratory animals and to exert a possible teratogenic effect (i.e., to cause severe fetal defects), led to the processors' voluntary elimination of MSG from baby foods.

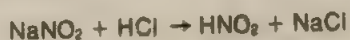
Additives That Retard Spoilage

Food spoilage can result from the growth of molds (fungi) or bacteria. Propionic acid and its sodium and calcium salts are added to bread and cheese to act as mold and yeast inhibitors. Sorbic acid, benzoic acid, and their salts are used also. The structures of some of these inhibitors are shown in **figure 17.3**.

Some inorganic compounds also are used as spoilage inhibitors. Sodium nitrite (NaNO_2) is used in the curing of meat. It serves to maintain the pink color of smoked hams, frankfurters, and bologna. Nitrites also contribute to the tangy flavor of processed meat products.

Nitrites are particularly effective as inhibitors of *Clostridium botulinum*, the bacterium that produces botulism poisoning. However, only about 10% of the amount used to keep meat pink is needed to prevent botulism. Sodium nitrate (NaNO_3) also has been used in curing meat. The Food and Drug Administration moved to ban the use of nitrates since they have no advantage over nitrites. At any rate, bacteria in our stomachs readily reduce nitrates to nitrites.

Nitrites have been investigated as possible causes of cancer of the stomach. In the presence of the hydrochloric acid (HCl) in the stomach, nitrites are converted to nitrous acid.



The nitrous acid then may react with compounds called secondary amines to form nitroso compounds

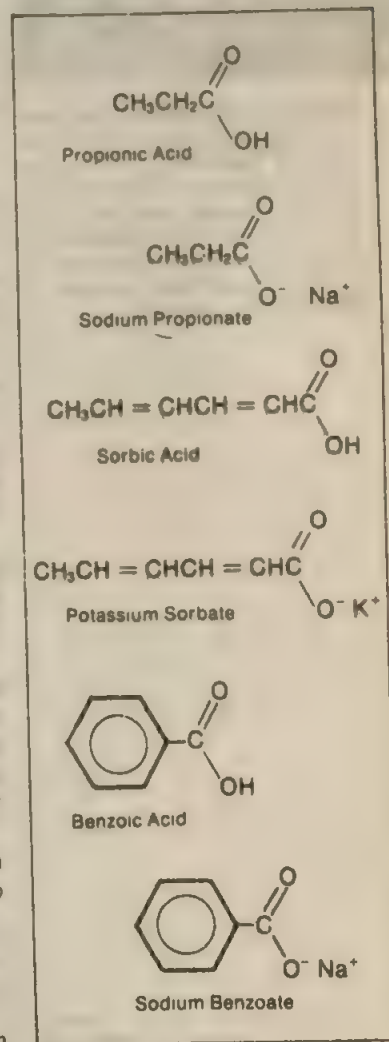


Figure 17.3 Some spoilage inhibitors.

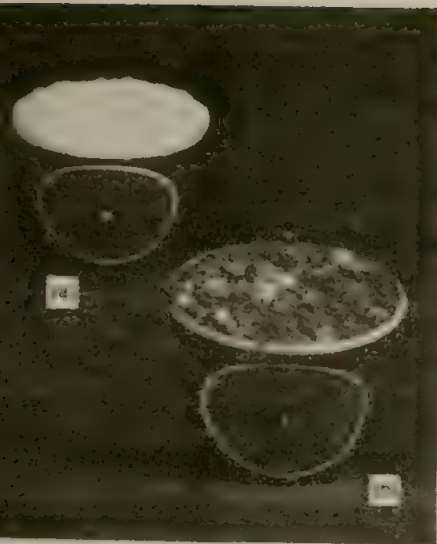
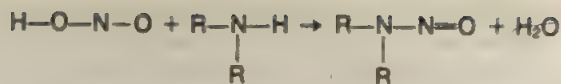


Figure 17.4 The addition of sorbates to cottage cheese can extend the product's shelf life by 30 or more days. (a) A sample containing 0.1% potassium sorbate stored for 3 days at 27°C. (b) A sample containing no sorbate stored for the same period at the same temperature. (Courtesy of Monsanto Co., St. Louis.)



Nitrous acid A secondary amine A nitroso compound

The R— groups may be alkyl groups such as methyl (CH_3-) or ethyl (CH_3CH_2-) or they may be more complex. In any case, these nitroso compounds are among the most potent carcinogens known. By eating foods containing nitrates and nitrites, we may be giving our stomachs the raw materials for cancer. It is a fact that the rate of stomach cancer is much higher in people in countries that use prepared meats than in the backward nations where people eat little or no cured meat. In 1978, nitrites themselves were shown to cause cancer in rats. The Food and Drug Administration moved to remove nitrites as food additives, and research efforts to find a suitable substitute preservative were intensified.

Another hazard associated with nitrates and nitrites is the disease *methemoglobinemia*, an oxygen-deficiency disease. This problem is particularly pronounced in infants. To date, it has been associated more with nitrates in well water than in foods. In that context, it is discussed more fully in chapter 18.

Sulfur dioxide (SO_2) is another inorganic food additive. A gas at room temperature, sulfur dioxide serves as a disinfectant and preservative, particularly for dried fruits such as peaches, apricots, and raisins. It also is used as a bleach that prevents the browning of some wines, corn syrup, jelly, dehydrated potatoes, and other foods.

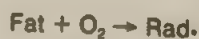
Sulfur dioxide seems safe when ingested with food. However, it is a powerful respiratory irritant when inhaled. It is a damaging ingredient of polluted air in some areas (chapter 19).

The Butylated World of Antioxidants

Antioxidants are added to foods mainly to prevent fats and oils from turning rancid and making the food unpalatable. Packaged foods (such as bread, potato chips, sausage, and dry breakfast cereals) that contain vegetable oils or animal fats most likely have antioxidants added.

Two compounds often used as antioxidants are butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT). Both are phenols, that is, compounds with a hydroxyl group ($-\text{OH}$) directly attached to a benzene ring. The structures of the two common antioxidants and the parent compound phenol are illustrated in **figure 17.5**.

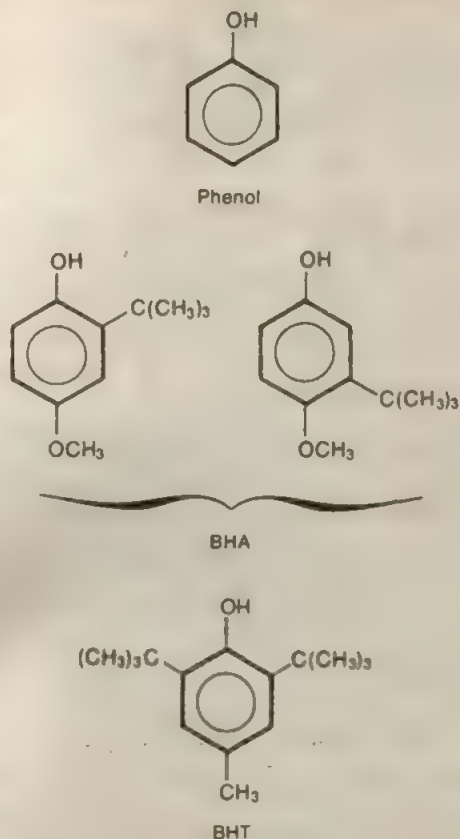
Fats turn rancid, in part, through oxidation. This process occurs through the formation of molecular fragments called *free radicals*. These fragments have an unpaired electron as a distinguishing feature. (Recall from chapter 5 that covalent bonds are shared pairs of electrons.) We need not concern ourselves with the details of the structures of radicals, but we can summarize the process. First, a fat molecule reacts with oxygen to form a free radical (which we will call Rad.).



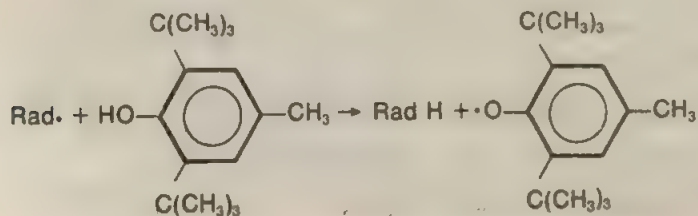
Then, the radical reacts with another fat molecule to form a new free radical that can repeat the process. A reaction such as this, in which intermediates are formed that keep the reaction going, is called a *chain reaction*. One molecule of oxygen leads to the decomposition of lots of fat molecules.

To preserve foods containing fats, processors package the product in a way that excludes air. However, it isn't possible to exclude air completely, and so chemical

Figure 17.5 Two common antioxidants are chemically related to phenol. BHA is a mixture of two isomers.

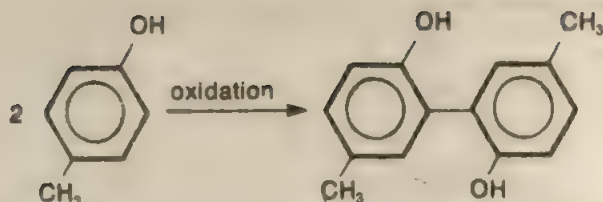


antioxidants are used to stop the chain reaction. They do so by reacting with the free radicals.



The new radical formed from BHT is rather stable. The unpaired electron doesn't have to stay put on the oxygen atom but can move around in the electron cloud of the benzene ring. The BHT radical doesn't react with fat molecules, and the chain is broken.

Why the butyl groups? Without them, the phenols would simply couple when exposed to an oxidizing agent.



With the bulky butyl groups aboard, the rings can't get close enough together for coupling. They are free, then, to trap free radicals from the oxidation of fats.

Many food additives have been criticized as harmful to people. BHA and BHT are no exceptions. These additives have been reported to cause allergic reactions in some people. Pregnant mice fed a diet containing 0.5% of either BHA or BHT give birth to offspring with chemical abnormalities in their brains. The Food and Drug Administration is conducting further studies of both additives.

Not all reports about the antioxidants have been unfavorable, however. BHT may have a serendipitous effect. When relatively large amounts of BHT were fed to rats daily, their life spans were increased by a human equivalent of 20 years. One theory about aging is that aging, like the rancidity of fats, is caused in part by the formation of free radicals. BHT retards this chemical breakdown in the cells in the same way that it retards spoilage in foods. The discovery of the secret of aging might lead to longer life spans for humans. Perhaps even more promising, however, is the possibility of eliminating some of the more deleterious effects of aging. In the laboratory, BHT also has shown antitumor activity. Some scientists have speculated that the increased use of antioxidants as food additives has contributed to a decline in the number of cases of stomach cancer in the United States.

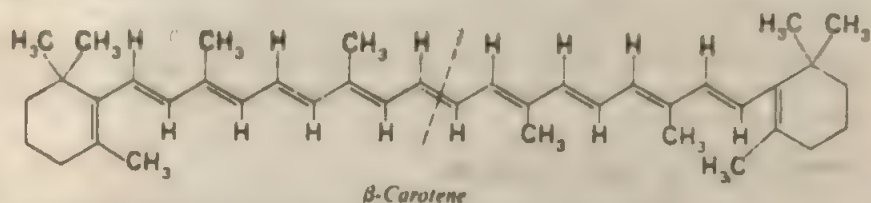
BHA and BHT are totally synthetic chemicals. There are natural antioxidants. Perhaps the most notable of these is vitamin E. The structure of this compound is given in table 16.5. Notice that vitamin E is also a phenol, with lots of substituents on the benzene ring. Presumably, its action as an antioxidant is quite similar to that of BHT.

Rats deprived of vitamin E become sterile. Because of this, vitamin E is called the antisterility vitamin. Some food faddists promote the ingestion of large amounts of vitamin E to increase sexual prowess, combat wrinkled skin, and prevent heart attacks. There is no unambiguous evidence for any of these claims. Just because vitamin E, in small amounts, prevents sterility in rats does not mean that we can assume that massive dosages will enhance sexual activity in humans.

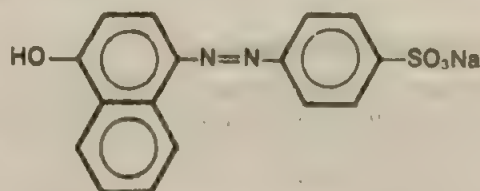
As we saw in chapter 16, vitamin E is available in wheat germ oil, green vegetables, vegetable oils, egg yolks, and meat. Most nutritionists contend that it would be nearly impossible to eat a diet deficient in vitamin E. Vitamin E is fat soluble and is stored in the body. Large doses may waste money, but they do not seem to have harmful effects. Their belief in the efficacy of vitamin E, however, might lead people to postpone medical treatment that they need.

A vitamin E deficiency can lead to a vitamin A deficiency. Vitamin A can be oxidized to a nonactive form when vitamin E is no longer present to act as an antioxidant. Indeed, the loss of vitamin E's antioxidant effect is believed to be responsible for all of the symptoms of vitamin E deficiency. Polyunsaturated fatty acids, especially, are oxidized at increased rates. Muscular dystrophy, sterility, and other symptoms manifested by animals deficient in vitamin E are believed to result from this "simple" change in body chemistry.

carotene (read *beta*-carotene) occurs in carrots. β -Carotene is used as a color additive in other foods, such as butter and margarine. (Our bodies convert β -carotene to vitamin A; thus, it is a vitamin additive as well as a color additive.) Other natural food colors include beet juice, grape hull extract, and saffron (from safflowers).



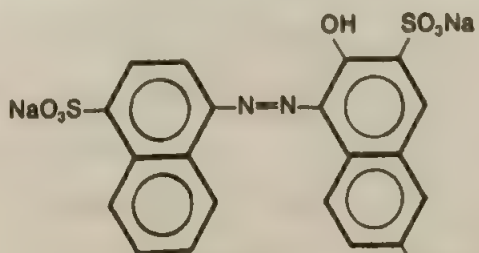
We have come to expect many foods to have characteristic colors. The food industry, to increase the attractiveness and acceptability of its products, has used synthetic food colors for decades. Since the Food and Drug Act of 1906, the Food and Drug Administration has regulated the use of these coloring chemicals and set limits on their concentrations. But the Food and Drug Administration is not infallible. Colors once on the approved list later were shown to be harmful and subsequently were removed from the list. In 1950, a candy company tried to duplicate in candy for Halloween the bright orange color of pumpkins. They used a large amount of Food, Drug, and Cosmetic (FD&C) Orange no. 1. Although this color had been safe in the amounts previously used, it caused severe gastrointestinal upsets in a number of trick-or-treaters. It was banned by the Food and Drug Administration.



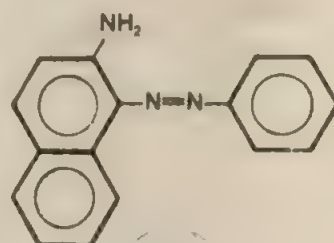
FD&C Orange no. 1

A few years later, two more dyes were banned. FD&C Yellow nos. 3 and 4 were found to contain small amounts of β -naphthylamine, a carcinogen. Furthermore, the dyes reacted with acids in the stomach to produce more β -naphthylamine. This compound induces cancer of the bladder in laboratory animals. Any chemical shown to induce cancer in laboratory animals is automatically banned under the 1958 Delaney Amendment to the Food and Drug Act.

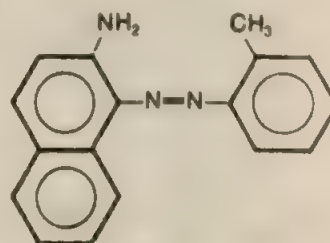
Several other dyes have since been banned, including FD&C Red no. 2, which was "delisted" in 1976 after it was shown to cause cancer in laboratory animals.



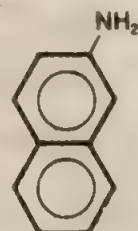
FD&C Red no. 2



FD&C Yellow no. 3



FD&C Yellow no. 4



β -Naphthylamine

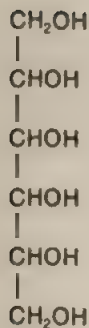
It should be noted that food colorings, even those that have been banned, present an extremely low hazard. They have been used for years with apparent safety. But, even if the hazard is low, there is essentially no benefit from food colors, other than an aesthetic one. Perhaps it would be best to ban these chemicals rather than to assume the risk, however small.

There are only a few artificial food colors still approved by the Food and Drug Administration. Several of these are being studied for possible harmful effects. Any food that contains artificial colors is supposed to be so labeled. You could avoid them if you wanted to.

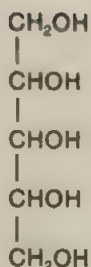
Sweet Chemicals: Sugar Substitutes

Recall from chapter 16 that sugars are polyhydroxy compounds. Indeed, many compounds with hydroxyl groups on adjacent carbon atoms are sweet. Even ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) is sweet, though it is quite toxic. Glycerol, obtained from the hydrolysis of fats (chapter 16), is also sweet. It is used as a food additive; however, it is used principally for its properties as a *humectant* (moistening agent), not as a sweetener.

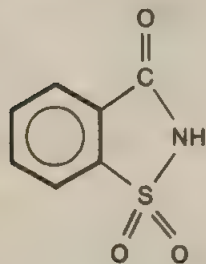
Other polyhydroxy alcohols are used as sweeteners, too. The most common of these is *sorbitol*, made by the reduction of glucose. Another is *xylitol*, which has five carbon atoms with a hydroxyl group on each. These compounds, though not strictly carbohydrates, have about the same Calorie content per gram. They have an advantage over sugars in that they are not broken down in the mouth and so do not contribute to tooth decay as the sugars do. This makes these alcohols useful in sugar-free chewing gums. In larger amounts, as in candies, sorbitol and xylitol often cause diarrhea.



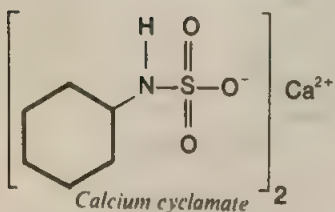
Sorbitol



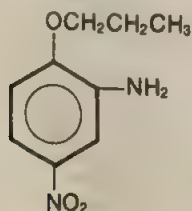
Xylitol



Saccharin



Calcium cyclamate



P-4000

Sweet Chemicals: The Artificial Sweeteners

Obesity is a major problem in most of the developed countries. Presumably, we could reduce the intake of Calories by replacing sugars with noncaloric sweeteners. It seems, though, that people who drink diet pop instead of that sweetened with sugar replace those Calories with others and still fail to lose weight. In spite of the fact that there is no evidence that artificial sweeteners are of any value in controlling obesity, they have become part of our culture.

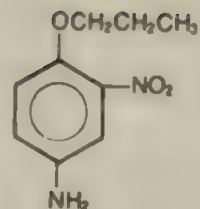
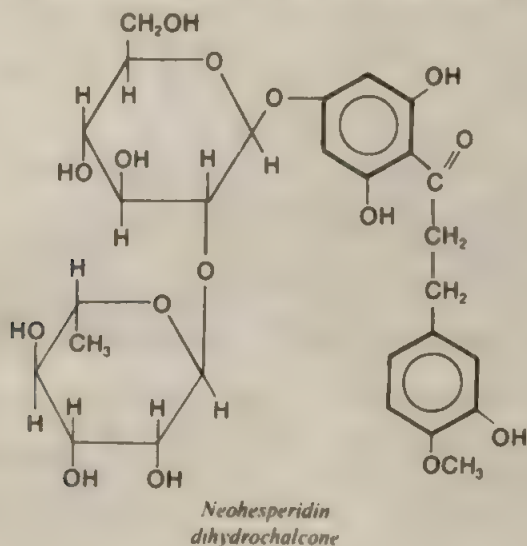
For many years, the major artificial sweeteners were saccharin and the cyclamates. In 1970, after studies showed that cyclamates caused cancer in laboratory animals, those sweeteners were banned. Subsequent studies have failed to confirm the original finding that cyclamates cause cancer. Nevertheless, the Food and Drug Administration has not lifted the ban.

In 1977, saccharin was shown to cause bladder cancer in laboratory animals. The Food and Drug Administration's move to ban saccharin was blocked by the Congress because saccharin was the last approved artificial sweetener. Its ban would have meant the end of diet pop and low-Calorie products.

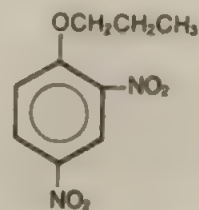
Table 17.3 compares the sweetness of a variety of substances. What makes a compound sweet? There is little structural similarity among the compounds. Saccharin, the cyclamates, and compound P-4000 bear little resemblance to the sugars. Even more baffling are the tastes of two compounds that closely resemble P-4000. Compound I, which has the NO_2 and NH_2 groups reversed, is tasteless. Compound II, which has two NO_2 groups, is extremely bitter. P-4000 is one of the sweetest substances known. In 1974, its use in the United States was banned because of its possible toxic effects.

Chemists continue to study the theory of what makes chemicals taste sweet (see reference 7). They also are pursuing applied research in the isolation, identification,

and synthesis of sweeteners. Perhaps the most promising compound they have come up with so far is neohesperidin dihydrochalcone. Its structure is almost as complicated as its name. It is derived from naringen, a compound that occurs naturally in grapefruit peels. Neohesperidin dihydrochalcone is 1000 times sweeter than sucrose and 20 times sweeter than saccharin. It is currently undergoing tests to determine whether it is safe to use. It may well replace saccharin if it passes the tests.



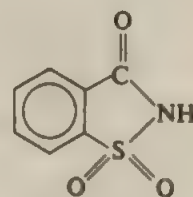
Compound I (tasteless)



Compound II (bitter)

Table 17.3
Sweetness of some compounds relative to sucrose as 100

<i>Compound</i>	<i>Relative Sweetness</i>
Glucose	74
Fructose	173
Galactose	70
Lactose	16
Sucrose	100
Maltose	33
P-4000	400 000
Saccharin	300



Saccharin

Smoking Additives Off the GRAS List

Some food additives have been used for many years without apparent harmful effects. In 1958, the United States Congress established a list of the additives "generally recognized as safe." This compilation became known as the *GRAS list*. Recent developments have brought to light some deficiencies in the original testing procedures. New research findings—and greater consumer awareness—have led the Food and Drug Administration to begin to reevaluate all the chemicals on the list.

Saccharin, the cyclamates, and several of the food colors now banned were once on the GRAS list. However, improved instruments and better experimental designs

have revealed possible harm where none was before thought to exist. Most of the newer experiments have involved feeding massive doses of the additives in question to laboratory animals, and they have been criticized in that regard. We discuss these testing procedures further in chapter 24.

Poisons in Your Food

People have been trying to deal with poisons in their food for millennia. Early foragers learned—probably by the painful process of trial and error—that some plants and animals were poisonous. We are all familiar with the fact that some mushrooms are poisonous. Rhubarb leaves contain toxic oxalic acid. The Japanese relish a variety of puffer fish that contains a deadly poison in its ovaries and liver. More than a hundred Japanese people die each year from improperly prepared puffers. The most toxic substance known is the toxin produced by the bacterium *Clostridium botulinum*. This organism grows in improperly canned food by a perfectly natural process. If the food isn't properly sterilized before it is sealed in jars or cans, the microorganism flourishes in the anaerobic (without air) conditions. The poison it produces is so toxic that 1 g of it could kill more than a million people.

The point to all this is that a food is not inherently good simply because it is natural. Neither is it necessarily bad because a chemical substance has been added to it.

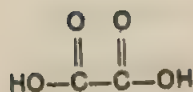
There's no doubt that we would get better nutrition if we ate nothing but fresh food. For people in large cities, that might well be impossible. And for everyone: who wants to spend all the time it takes to gather fresh food and prepare every item for every meal from scratch? Convenience foods are indeed convenient. Food additives help them to be easier to fix, more attractive, and (in some cases) more nutritious.

Cancer in Your Diet?

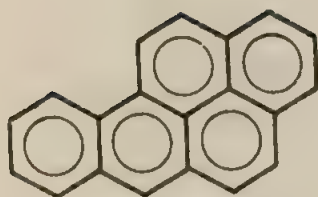
There is little chance that we will suffer acute poisoning from approved food additives. But what about cancer? Could all those chemicals in our food increase our risk of cancer? The possibility exists, even though the risk of it may be very low.

We should recognize, though, that carcinogens occur in food naturally, too. A charcoal-broiled steak contains 3,4-benzpyrene, a carcinogen also found in cigarette smoke and automobile exhaust fumes.* Cinnamon and nutmeg contain safrole, a carcinogen that has been banned as a flavoring in root beer.

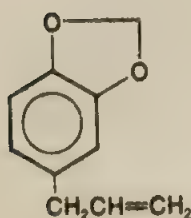
Among the most potent carcinogens are the *aflatoxins*, compounds produced by molds growing on stored peanuts and grains. Aflatoxin B₁ is estimated to be 1



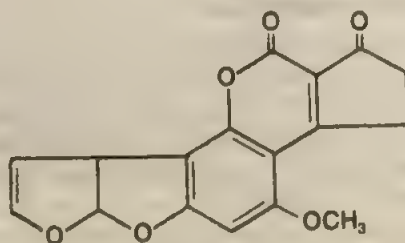
Oxalic Acid



3,4-Benzpyrene



Safrole



Aflatoxin B₁

*It should be recognized that there is a great difference between ingesting carcinogens (with food) and inhaling them (with cigarette smoke or polluted air). A compound that could induce lung cancer might be harmless in the stomach.

million times as potent a carcinogen as saccharin. And there is no way to keep it completely out of our food. The Food and Drug Administration sets a tolerance of 20 ppb for aflatoxins.

Should we ban steaks, spices, peanuts, and grains because they contain naturally occurring carcinogens? Probably not. The risk is slight, and life is filled with more serious risks. Should we ban food additives that have been shown to be carcinogenic? Probably, yes. Why take the risk, however slight, when it is easy to avoid?

Incidental Additives

A variety of chemical substances may be present in foods as a result of carelessness or accident in some phase of production, processing, storage, and packing. These incidental additives often receive wide publicity. In 1959, the sale of cranberries was forbidden after some shipments were found to be contaminated by the weed killer aminotriazole, a compound shown to be carcinogenic in tests on laboratory animals. In 1969, Coho salmon taken from Lake Michigan were shown to contain DDT above the tolerance level. Sale of these fish was banned, also. In 1970, fish taken from the Detroit River and Lake St. Clair (between Michigan and Ontario) were found to be contaminated with methylmercury (chapter 18). Mercury compounds also were found in fish taken from the Wisconsin River and other inland waters. Commercial fishing was banned in areas in which substantial mercury contamination was found. Polychlorinated biphenyls (PCBs, chapter 14) have been found in poultry and eggs. These products, too, were seized and destroyed. Related compounds, polybrominated biphenyls (PBBs), meant to be used as fire-retardants, were accidentally mixed with animal feed in western Michigan. Many farm animals were destroyed, and still PBBs got into the food supply. Nearly all the residents of Michigan now have PBBs in their bodies.

Chemical substances in feeds for animals often show up in the meat we eat. Antibiotics are added to animal feed to promote weight gain. Residues of these have been found in up to 25% of the animals slaughtered. These residues may result in sensitization of individuals who eat the meat, thus hastening their development of allergies. Antibiotic residues in meat also may hasten the process by which bacteria become drug resistant.

Diethylstilbestrol (DES), a synthetic female hormone (chapter 22), also has been added to animal feeds to promote weight gain. It was banned in 1973 after evidence surfaced that showed that it caused vaginal cancer in the daughters of women who had taken DES during pregnancy. The ban was lifted by court action, but it was reinstated in 1979.

Note that the effect of DES did not show up for 15 years. Even then it appeared in the offspring of the women who took the drug. This points out some of the problems involved in evaluating a chemical for its possible harmful effects.

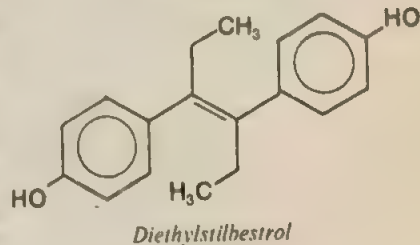
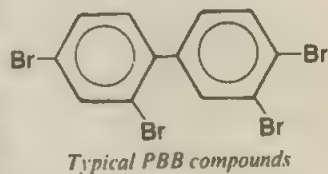
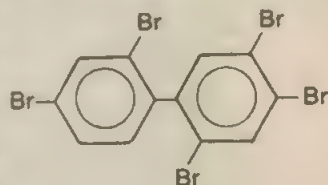
A World without Food Additives?

Could we get along without food additives? Some of us could. But food spoilage might drastically reduce the food supply in an already hungry world. And diseases due to vitamin and mineral deficiencies might flourish again. Foods might cost more and be less nutritious. Food additives seem to be a necessary part of our modern society.

It is true that there are hazards associated with the use of some food additives. Such hazards should be minimized. What should we do? We should be sure that the Food and Drug Administration is staffed with qualified personnel to ensure the adequate testing of proposed food additives. People trained in chemistry are necessary for the control and monitoring of food additives and the detection of



Figure 17.6 Aflatoxins, highly carcinogenic compounds, are produced by molds that grow on peanuts and stored grains. (Courtesy of Waters Associates, Milford, MA.)



contaminants. Research in the analytical techniques necessary for the detection of trace quantities is vital to adequate consumer protection. We also should work for laws adequate to prevent the unnecessary and excessive use of pesticides and other agricultural chemicals that might contaminate our food. Above all, we should be alert and informed on these problems so vital to our health and well-being.

Problems

1. What is a food additive? What are the two broad types of food additives? Give an example of each.
2. List five functions of food additives.
3. Why are more food additives used today than in 1900? List three reasons.
4. What is the function of each of the following food additives?
 - a. potassium iodide d. sodium nitrite g. BHA
 - b. vanilla extract e. potassium sorbate h. FD&C Yellow no. 5
 - c. MSG f. sulfur dioxide i. saccharin
5. What is the difference between vanilla extract and imitation vanilla flavor?
6. What is enriched bread? Is it equal in nutritional value to bread made from whole grain?
7. Consult a recent issue of the *FDA Consumer* and make a list of incidental additives found in foods and reported in that issue. What are the most common causes of contamination?
8. Examine the label on a sample of each of the following.
 - a. a can of pop c. a dried soup mix e. a can of fruit drink
 - b. a can of beer d. a can of soup f. a cake mix
 Make a list of the food additives in each. Try to determine the function of each additive.
9. Maraschino cherries are bleached (with sulfur dioxide) and then dyed with an organic food coloring. Do you think consumers would buy the uncolored cherries?
10. One step in the production of raisins involves the treatment of grapes with sodium hydroxide (NaOH). This compound is also known as caustic soda or lye. Some raisins then are bleached with sulfur dioxide to remove their color. Would you expect to find these "golden" raisins in an organic food store?
11. What does each of the following acronyms stand for? Discuss the importance of each in the study of food additives.
 - a. BHT d. GRAS
 - b. DES e. MSG
 - c. FDA f. PBBs
12. Which additional food additives (if any) should be banned? Which should be further restricted? Explain your answers fully.

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chapter 18

Water: To Drink and to Dump Our Wastes In

In chapter 9, we considered some of the unusual properties of water. The presence of water on Earth makes our planet unique in the solar system; most likely, it is the only planet capable of supporting life. Should we someday search for life outside our solar system, we probably would look for a watery planet.

Those properties of water that make it uniquely suited to the support of life also make it easy to pollute. Many chemical substances are soluble in water. Thus, they are easily dispersed and eventually are scattered to nearly infinite dilution in the ocean. This scattering is in accord with the natural tendency toward maximum entropy as described by the second law of thermodynamics (chapter 12). Removing these chemicals from our water supplies, once they are there, requires often enormous expenditures of energy.

In this chapter, we discuss water pollution, wastewater treatment, and water treatment. Don't underestimate the importance of good, clean drinking water. We could live for nearly a month without food. Without water, we would last only a few days at best.

Some Biblical Chemistry

A dependable supply of fresh water has long been a problem. When Moses led the Israelites out of Egypt into the wilderness, they encountered a desert area where potable water was scarce. While nearly everyone knows the Biblical account of how Moses struck the rock to bring forth water, an incident at Marah is less well known. At Marah, the Israelites couldn't drink the water because it was bitter. According to the account in Exodus, God commanded Moses to throw a tree into the water to purify it.

Biological Contamination: Ancient and Deadly

The pollutants in the waters of Marah were natural ones. Early people did little to pollute the water and the air, if only because their numbers were so few. It was with the coming of the agricultural revolution and the rise of cities that there were

* Recall from chapter 7 that one property of basic solutions is that they are bitter. The water at Marah was probably basic, or *alkaline*. Such alkali waters are common in desert areas. Attempts have been made to give a chemical explanation of Moses' purification of the brackish water. The tree was probably a dead one, long bleached by the desert sun. Such bleaching oxidizes the alcohol groups in cellulose to carboxylic acid groups.



These acidic groups serve to neutralize the alkali in the water.

Moses didn't have to understand the science of water purification. He merely applied the appropriate technology.



Figure 18.1 An adequate supply of water is essential to life. In this photograph, a tubewell in a Yemeni village provides water for drinking, crop irrigation, bathing, and laundry. (Courtesy of Food and Agriculture Organization of the United Nations, Rome.)

Figure 18.2 Life becomes difficult without an adequate supply of water. This photograph shows a dry riverbed that became a graveyard for cattle when a drought struck the African Sahel. (Courtesy of the Nancy Palmer Photo Agency, New York. Photo by Florita Botts.)

enough *Homo sapiens* to pollute the environment seriously. Even then, the pollution was mostly local and largely biological. Human wastes were dumped on the ground or into the nearest stream. Disease organisms were transmitted through food, water, and direct contact.

Contamination of water supplies by microorganisms from human wastes was a severe problem throughout the world until about a hundred years ago. During the 1830s, severe epidemics of cholera swept the Western World. Typhoid fever and dysentery were common. In 1900, for example, there were over 35 000 deaths from typhoid in the United States. Today, as a result of chemical treatment, municipal water supplies in the advanced nations are generally safe. However, water-borne diseases are still quite common in much of Asia, Africa, and Latin America. Indeed, it is estimated that "80 percent of all the world's sickness is caused by contaminated water" (reference 2).

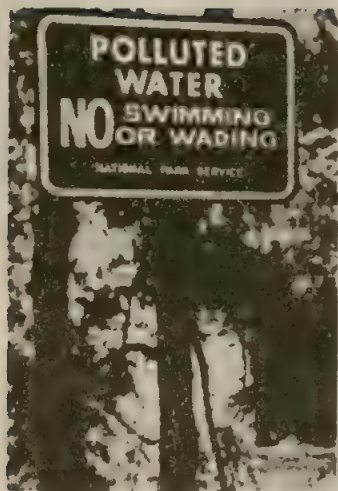


Figure 18.3 A sign of the times, all too common near our lakes and streams. (Courtesy of Ward's Natural Science Establishment, Inc.)

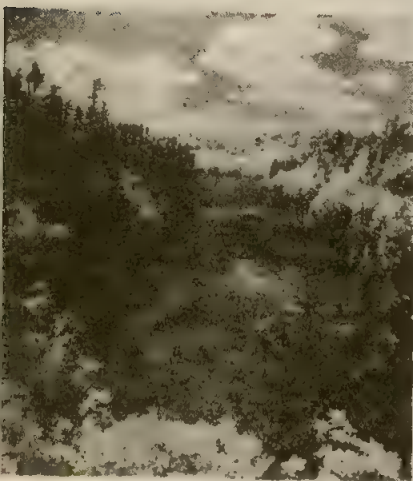


Figure 18.4 The St. Croix River, as yet a relatively unpolluted river. (Courtesy of the Wisconsin Department of Natural Resources, Madison.)

The threat from biological contamination has not been totally eliminated from the United States. In 1969, the Community Water Supply Study estimated that 8 million people drank water from 5000 contaminated water-supply systems. Hepatitis (a viral disease occasionally spread through drinking water) at times threatens to reach epidemic proportions, even in the most advanced nations.

Biological contamination also lessens the recreational value of water. Swimming is forbidden in many areas (**figure 18.3**). The Mississippi River is so badly polluted in certain stretches that picnics along the banks are forbidden lest people become ill from the contaminated spray. By the late 1960s, Lake Erie was being described as "America's Dead Sea" and "the world's largest cesspool." Polluted waters were not unique; unpolluted ones were. The St. Croix River (**figure 18.4**), which forms part of the border between Wisconsin and Minnesota, was described as the *only* major unpolluted river in the United States near a sizable metropolitan area (Minneapolis-St. Paul).

The 1970s brought a good deal of improvement in many waters. Fish life thrives again in Lake Erie. Beaches on Lake Michigan near Chicago, closed in 1969 because of pollution, were reopened in 1975. The Mississippi below Minneapolis-St. Paul has been reopened to recreation and swimming after being closed for many years. Shellfish are being harvested again in Maine's Belfast Bay. Shrimp and oysters are returning to Escambia Bay off Pensacola, Florida. Atlantic Salmon have returned to the Connecticut River for the first time in 100 years. And, in England, fish once again inhabit the Thames.

Despite all the good news, pollution from domestic sewage remains the gravest threat to the water supply in the United States. We still have a long way to go.

Chemical Contamination: From Farm, Factory, and Home

The industrial revolution added a new dimension to our water-pollution problems. Factories often were built on the banks of streams, and chemicals and other wastes from them were dumped into the streams to be carried away. The rise of modern agriculture also has led to increased chemical contamination as fertilizers and pesticides have found their way into the water system. Transportation of petroleum results in oil spills in oceans, estuaries, and rivers. Acids enter the waterways from mines and factories. Household chemicals also contribute to water pollution when detergents, solvents, and other chemicals are dumped down drains.

We consider the various aspects of water pollution in later sections of this chapter. First, though, let's look at water as it occurs in nature.

Natural Water Isn't All H_2O

Rainwater carries dust particles from the atmosphere to the ground. Rainwater also dissolves a little oxygen (O_2), nitrogen (N_2), and carbon dioxide (CO_2) as it falls through the atmosphere. During electrical storms, lightning causes nitrogen, oxygen, and water vapor to combine to form nitric acid (HNO_3). Traces of this, too, are found in rainwater.

As water moves along or beneath the surface of the Earth, it dissolves minerals and matter from decaying plants and animals. Recall that minerals (salts) are ionic and that ions have either positive or negative charges. The principal positive ions in natural water are sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), and sometimes iron (Fe^{2+} or Fe^{3+}). The negative ions are usually sulfate (SO_4^{2-}), bicarbonate (HCO_3^-), and chloride (Cl^-). The presence of calcium, magnesium, and iron salts in the water supply makes the use of soap inconvenient. Water containing these ions is called *hard water*. The positive ions react with the

negative ions in soap (chapter 20) to form a scum that clings to clothes and leaves them dingy-looking. This scum is also responsible for the familiar bathtub ring.

Sewage: Some Chemistry and Biology

Pathogenic (disease-causing) microorganisms are not the only problem caused by dumping human sewage into our waterways. The breakdown of organic matter by bacteria depletes the dissolved oxygen in the water and enriches it with plant nutrients. When there is only a small amount of waste, a stream can handle it without difficulty. But, when massive amounts of raw sewage are dumped into a waterway, undesirable changes result.

Most organic material can be broken down (degraded) by microorganisms. This biodegradation can be either *aerobic* or *anaerobic*. Aerobic oxidation occurs in the presence of dissolved oxygen. Oxidation of organic matter results in the depletion of oxygen. A measure of the amount of oxygen needed for this degradation is the *biochemical oxygen demand* (BOD). The greater the quantity of degradable organic wastes, the higher the BOD. If the BOD is high enough, no life (other than odor-producing anaerobic microorganisms) can survive in the lake or the stream. Flowing streams can regenerate themselves. Rapid ones soon come alive again as oxygen is dissolved by the moving water. Lakes with little or no flow can remain dead for decades.

With adequate dissolved oxygen, aerobic bacteria (those that require oxygen) oxidize the organic matter to carbon dioxide, water, and a variety of inorganic ions [such as nitrates (NO_3^-), nitrites (NO_2^-), phosphates (PO_4^{3-}), sulfates (SO_4^{2-}), and bicarbonates (HCO_3^-).] The water is relatively clean, but the ions, particularly the nitrates and phosphates, may serve as nutrients for the growth of algae. These algal blooms cause problems, also. When the algae die, they become a part of the organic wastes and increase the BOD. Also, algal growth is stimulated by the runoff of agricultural fertilizers (chapter 15) and by the phosphates in detergents (chapter 20). This combination leads to dead and dying streams and lakes, which an overburdened nature cannot purify nearly as quickly as we can pollute.

When the dissolved oxygen in a body of water is depleted by too much organic matter—whether from sewage, dying algae, or other sources—degradation shifts to an anaerobic process. Anaerobic bacteria thrive in the absence of oxygen. Instead of oxidizing the organic matter, they reduce it. Sulfur is converted to hydrogen sulfide (H_2S) and to foul-smelling organic compounds such as methanethiol (CH_3SH). Nitrogen is reduced to ammonia and to odorous amines (chapter 11). The foul odors are a good indication that the water is overloaded with organic wastes. No life, other than the anaerobic microorganisms, can survive in such water.

How to Foul Up an Ecological Cycle

Let's consider water pollution from the point of view of a fish. Take a look at the much simplified ecological cycle in **figure 18.7**. Such a cycle in a more complicated form could take place in a small lake. Fish in the water produce organic wastes. Bacteria break down these wastes into inorganic materials. These inorganic materials serve as nutrients for the growth of algae. Fish eat the algae, balance is established, and the cycle is complete. This is a biological cycle, but chemistry can lend some insight into it by providing an understanding of the breakdown of materials, the processes of growth, and the role of nutrients.

Now let's look at some of the ways people can disrupt the cycle. We can increase the organic wastes by dumping sewage into the water. In breaking down these wastes, bacteria consume all the dissolved oxygen and the fish die. Chemists can monitor the BOD of the water, thus identifying the problem and gauging its severity.

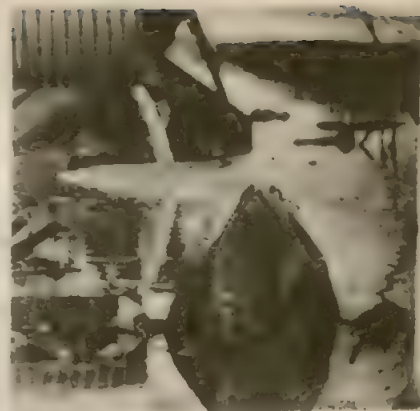


Figure 18.5 Common sewage from homes and businesses depletes the dissolved oxygen in water. (Courtesy of Henry H. Valukas, Minnesota Environmental Control Citizens Association, St. Paul.)



Figure 18.6 An algal bloom on a nutrient-enriched lake. (Courtesy of the Minneapolis Tribune, Minneapolis.)

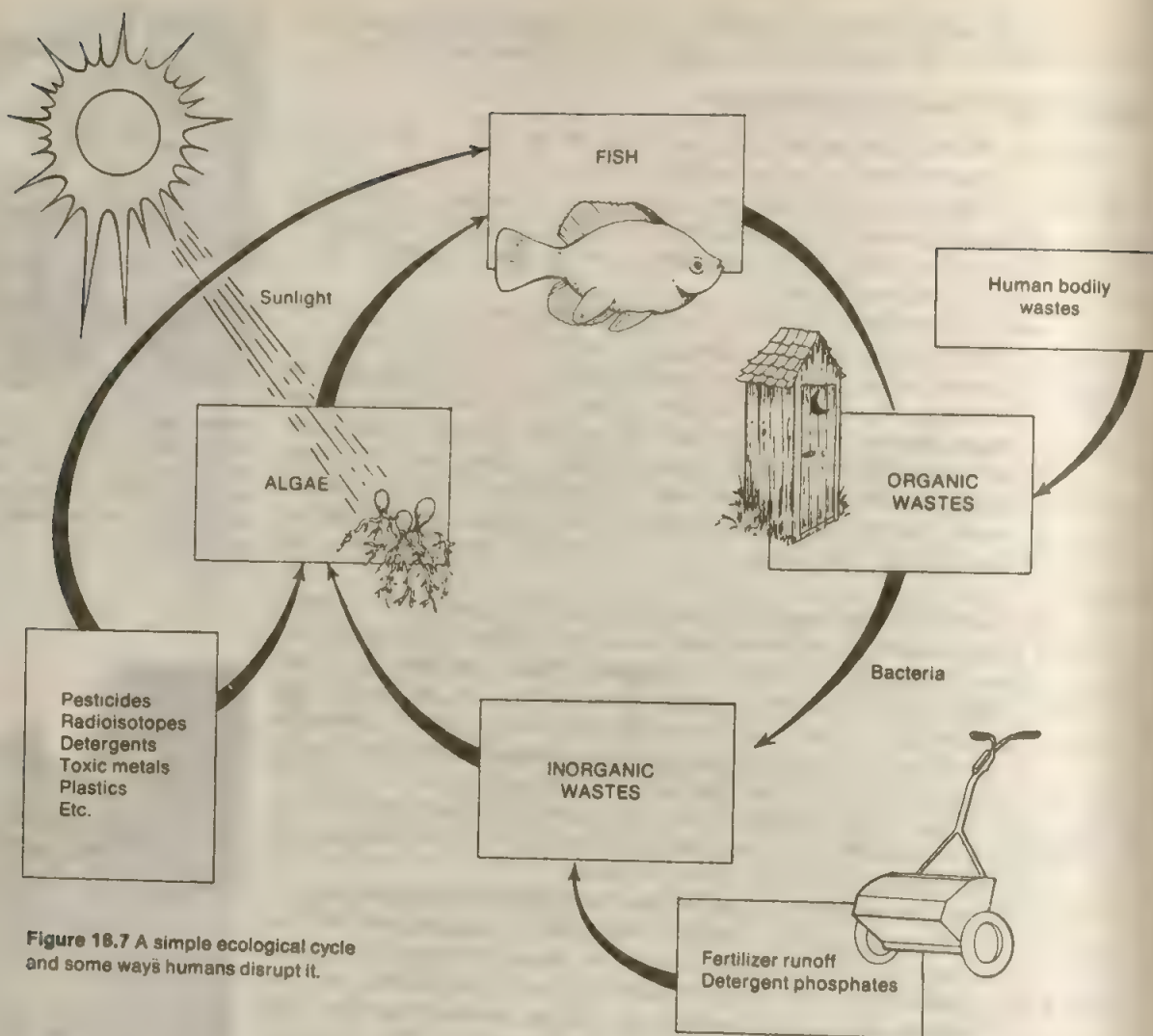


Figure 18.7 A simple ecological cycle and some ways humans disrupt it.

Chemists also can contribute to the development of better methods of wastewater treatment, as we see a bit later.

Dumping our sewage into the water isn't the only way we can foul up an ecological cycle. We can and do introduce phosphates from our detergents. Fertilizer runoff and seepage from feedlots add inorganic nutrients to the cycle, and an algal bloom can lead to oxygen depletion and death for the fish. Perhaps the most enigmatic influence of all, though, comes through the introduction of new substances into the ecological water cycle: pesticides, radioisotopes, detergents, toxic metals, plastics, et cetera.

By creating new materials, chemists have made a number of ecological problems possible. But chemists and chemistry are also necessary to any understanding of our pollution problems. It is only through the development of sophisticated analytical methods and instruments that we are even aware of some of our ecological problems. We worry about parts per billion of contaminants when even parts per million couldn't have been detected a few years ago. A stinking lake would be obvious to

everyone, but only a person trained in chemistry could determine the level of many dangerous, yet invisible, materials in the water we drink.

Everything Is Connected to Everything

Ecological cycles do not operate in isolation. The simple cycle described above is interwoven with many others. Figure 18.8 shows a cycle that occurs in the soil. Plants grow and then die and decay. The decayed matter, or *humus*, contributes to the porosity of the soil. It enables essential oxygen to reach the root cells of plants. Bacteria further break down the humus to inorganic fertilizers. These, in turn, nourish new plant growth in the soil, and the cycle is complete.

We disrupt this cycle by removing the plants as crops. This depletes the humus (and consequently the inorganic nutrients), and then synthetic fertilizers must be used to maintain crop yields. We have already seen how these fertilizers enter and disrupt ecological cycles in water. Depletion of humus also leads to decreased soil porosity and to increased erosion. Furthermore, after we eat the plants, the nutrients (our wastes) are not returned to the soil but are dumped into rivers and streams. Farming in America has become a process in which nutrients are removed from the soil and transported (eventually) to the sea. In the sea, the nutrients are diluted and they cannot be recovered without fantastic expenditures of energy. We are caught again by the second law (chapter 12).

Figure 18.8 A simple cycle of plant growth in the soil and some of the effects of modern farming on the cycle.

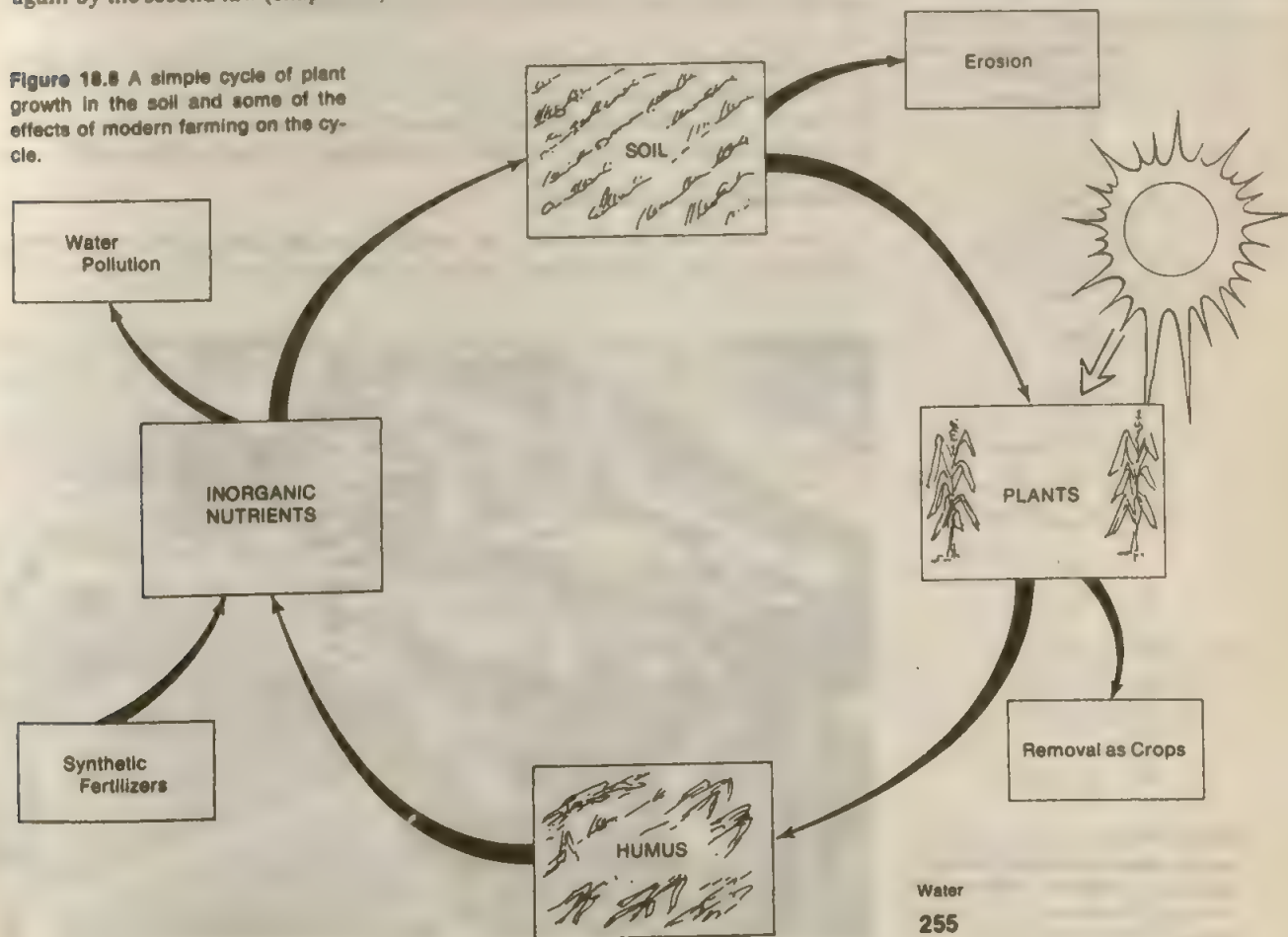




Figure 18.9 Acid forms in water draining from an abandoned mine. (Courtesy of Environmental Protection Agency and Documerica.)

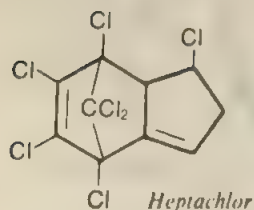
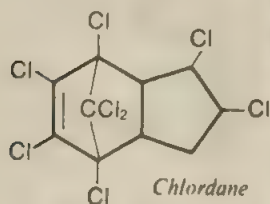
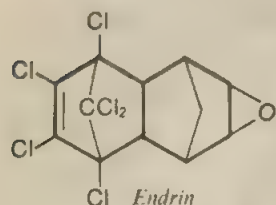


Figure 18.10 In 1969, a loss of 41 million fish was attributed to pollution. (Courtesy of Henry H. Valiukas, Minnesota Environmental Control Citizens Association, St. Paul.)

Contamination by Toxic Chemicals

A number of chemical substances—including fertilizers and detergents as well as the products of the breakdown of organic matter—enter our water system. Water also is contaminated by pesticides running off farmlands and suburban lawns, by acids draining from mines (**figure 18.9**), and by oil spilled and dumped. Cyanide compounds, phenols, toxic metals, organic solvents, and radioactive substances are found in the water in some parts of the country.

Many of these substances are relatively new as pollutants. Water- and waste-water treatment plants generally have not been designed to remove them from our drinking water. This means that we face new threats to the public health.

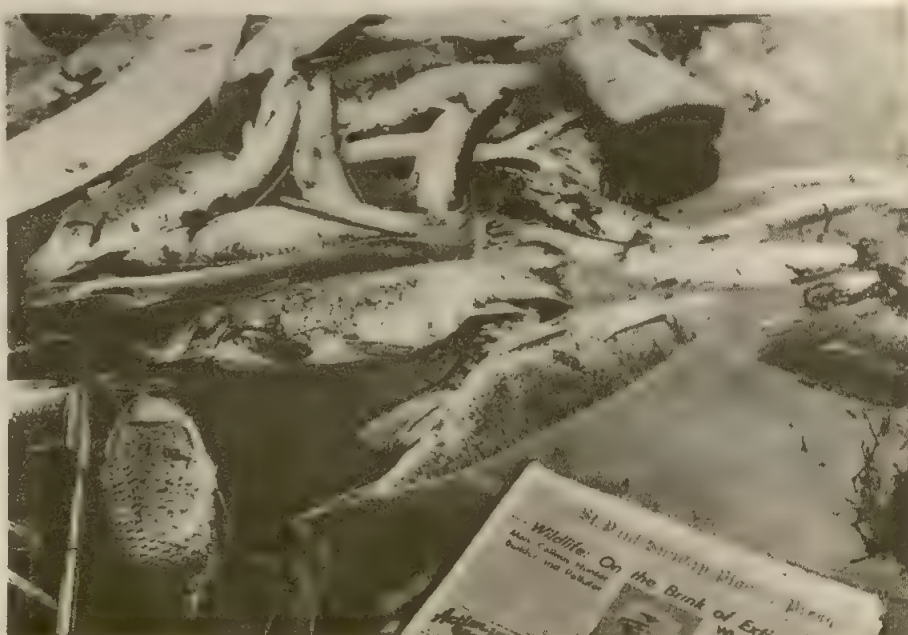
Pesticides on Tap

In chapter 15, we discussed some of the pollution problems associated with DDT. Many other pesticides and herbicides have been found in rivers, streams, and lakes, and even in the ocean. Massive fish kills have been caused by chlorinated hydrocarbon pesticides. The ghastly kill on the lower Mississippi River in 1963 was caused (presumably) by endrin, which was thought to have been dumped into the river by a chemical plant in Memphis. Although the case against the plant was never proved, close federal supervision of the plant has stopped the discharge of the pesticide into the river. Once the discharges had been stopped, the fish kills ended, too.

Low levels (in parts per billion) of endrin, chlordane, heptachlor, and other chlorinated hydrocarbons have been found in the municipal water supplies of a number of cities. The long-term effects on people of exposure to low levels of these chemicals are not known. In their physiological action, they are similar to DDT.

The Ecological Cost of Paper

Industries have made substantial progress toward the elimination of water pollution since the United States Congress passed the Water Pollution Control Act



Amendments in 1972. Nevertheless, in certain areas, industrial water pollution remains a significant problem. We can't examine all the different types of industrial water pollution here, but we can look at a few typical examples.

Let's look first at paper mills. Not only do paper products contribute in large part to the problems of litter and solid-waste disposal, they are products that take their toll on the environment as they are being manufactured.

Essentially, paper is a tangled mass of cellulose fibers. The main source of these fibers is wood. If we were totally conscious of the source of the paper we use—trees—we might waste a lot less of it.

In the manufacture of high-grade papers, lignin, a complex organic material in cellulose, is dissolved out by a bisulfite (HSO_3^-) solution. The process releases sulfur dioxide and other noxious gases. The odor emanating from a paper mill is often unmistakable—and unforgettable.

In the past, dissolved organic matter and either acidic sulfite chemicals or basic (alkaline) materials often were dumped into the nearest waterway. The BOD of the water was greatly increased, and there was no aquatic life in long stretches of the stream. Wastewater-treatment equipment is now used by most paper mills. Rapid improvement has been made in many areas, but we still have a long way to go in others. And the demand for paper is constantly increasing.

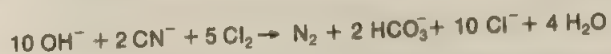
Research at the University of Nebraska has shown that the waste sulfite liquor from paper mills makes an excellent supplement for cattle feed. The waste from paper mills was found to be as effective in the feed ration as molasses, a much more expensive additive. This is certainly an encouraging example of the wise use of resources. The papermaker's trash may well become the cattle feeder's treasure.

The Ecological Cost of an Automobile

It takes about 900 kg of steel to make an average-size American automobile. To make that steel, it takes about 100 m³ of water. Only about 4 m³ are lost through evaporation. The remainder is polluted with acids (mainly hydrochloric acid), grease and oil, lime, and iron salts.

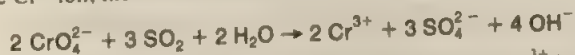
Chrome plating bumpers, grills, and ornaments is also a source of pollution. Waste chromium [in the form of chromate ions (CrO_4^{2-})] and cyanide ions (CN^-) are products of this process. In the past, these toxic substances were dumped into waterways. Nowadays, they generally are removed (at least partially) by chemical treatment.*

*Cyanide is treated with chlorine to form nitrogen gas, bicarbonate ions, and chloride ions.



It is true that the products of this treatment, bicarbonate and chloride, are still pollutants. These are much preferable, however, to the highly toxic cyanide.

Chromate is removed by reduction with sulfur dioxide. The chromium winds up as the Cr^{3+} ion, the sulfur as sulfate.



Sulfate is still a pollutant but generally not a serious one. Cr^{3+} is relatively insoluble in alkaline solution but is soluble enough in acidic media to constitute a problem.

Now, to get an automobile, add in the cost (environmental and economic) of elastomers for tires, PVC for a vinyl hard top, fabrics for upholstery, glass for windows, 520 kwh of electricity—the list goes on and on—and it is easy to see that the private automobile is an ecological disaster even before it hits the road. And once on the road, it is the major contributor to air pollution (chapter 19).

Other Industries Also Pollute

Most other industries also contribute to water pollution. Table 18.1 lists the water required (per metric ton) for the production of a variety of materials. Let's now look at some of the pollutants from various industries.

The textile industry dumps conditioners, dyes, bleaches, and water effluents containing oils, dirt, and other organic debris. Meat-packing plants dump blood, the contents of entrails, and other animal wastes. Other food-processing plants discharge fruit and vegetable skins, seeds, leaves, stems, and other vegetable wastes. Refineries release dyes, oils, acids, brines, sulfur compounds, and other wastes into waterways. Chemical plants produce a variety of waste materials. There are treatment methods available for processing most wastes, but the high cost of waste treatment makes some industries reluctant to use the technology available.

The 1972 amendments to the water-pollution-control legislation require more effective treatment of wastewater. By 1983, water in all navigable streams is supposed to be clean enough for swimming and recreation. By 1985, industries must have eliminated completely the discharge of pollutants.

Table 18.1
Water used (per metric ton*) for the production of various materials.

<i>Material</i>	<i>Water required (in cubic metres*)</i>
Steel	100
Paper	20
Copper	400
Rayon	800
Aluminum	1280
Synthetic rubber	2400

*A cubic metre of water weighs 1000 kg, or 11.

Heavy-Metal Contamination

A variety of heavy-metal poisons have been found in some of our waterways. Perhaps the most notable of these is mercury and its compounds. Mercury compounds have been found in canned tuna, frozen swordfish, and some river fish.

Mercury compounds enter the water environment in a variety of ways. Mercury compounds have long been used to prevent fungal infections, especially in seeds. Paper mills once used a mercury-based fungicide to prevent the growth of fungi and slime during the pulping process. This fungicide was found in the plants' discharge. Plants making chlorine and alkali (sodium hydroxide) were found to be discharging metallic mercury into the waterways. Many of these sources have been eliminated or their wastes reduced.

Not all the mercury in the environment has been put there by people. Volcanoes contribute a significant amount. The United States Naval Research Laboratory has

Figure 18.11 Heavy metals are defined as those having a density greater than 5.5 g per cubic centimetre. They are located at the lower center of the periodic chart. The symbols for several of the elements that pose environmental problems are indicated

found concentrations of mercury in the air over the new Hulgafell volcano in Iceland to be 100 times that in air over cities in the United States. High levels of mercury (although still not dangerous to humans) also were found in lava around volcanoes in Hawaii and Iceland. Such natural eruptions may add far more mercury to the environment than people do. But local pollution problems—from factories, farms, mines, and mills—still can be serious.

Finding mercury in fish came as quite a surprise. Chemists know that nearly all inorganic mercury compounds are insoluble. It had been assumed that whatever mercury did get into a stream would sink to the bottom and lie harmlessly in the sludge. To the surprise of nearly everyone, Swedish scientists discovered that certain bacteria could convert mercury to methylmercury, an extremely toxic chemical that is readily absorbed by plants and animals. Quick action was taken in most areas to prevent further mercury pollution. But the mercury that we have already introduced into the environment will be there for a long, long time.

Cadmium is another poisonous heavy metal. Cadmium ions (Cd^{2+}) sometimes are found in water. They get there from coal and zinc mining, from water pipes, from plastics factories, and from other industrial sources. Cadmium ions are quite similar to zinc ions (Zn^{2+}). Cadmium compounds often are found wherever zinc compounds are found.

Chromium, nickel, cadmium, and other metal ions enter the waterways when wastes from electroplating are dumped. Some old plumbing includes lead pipes, and lead ions enter drinking water from the pipes. (A section of Boston has lead water pipes.) Arsenic compounds from detergents and pesticides also get into our water.

These toxic metals and others enter our bodies through food and air as well as through water. We encounter lead as an air pollutant in the next chapter. And we discuss the toxicity of heavy metals in some detail in chapter 24.

An End to Water Pollution

Most of the technology needed to alleviate water pollution is available now. The cost of ending it will be high, but the cost of not ending water pollution would be higher. Every industrial plant in the United States will be required to clean up its own effluent, either in its own special treatment plant or in conjunction with a municipal sewage-treatment plant. Cities, towns, and villages—even rural areas—

will be required to construct adequate treatment plants. Federal law has set a goal of "zero discharge" by 1985. Even though zero discharge* is an absurd concept, we can have clean water for swimming, fishing, boating, and drinking if we are willing to pay the price. Let's turn our attention now to wastewater treatment plants to learn how they work and how they can be improved to meet our goal of clean water.

*Zero discharge is absurd for a number of reasons. First of all, it depends on the limits of chemical instrumentation. A few years ago, chemists would have found "zero" mercury in tuna simply because the instruments available could not detect levels of 0.5 ppm. Today, instruments can detect parts per trillion (or less) of some contaminants, but we could never be sure that there is "zero" pollutant there.

Another reason we could never reach "zero" levels of pollution in the water is that the cost of removing the last traces of pollutants would be astronomical. The argument is too complex to repeat in its entirety here, but it is a matter of orders of magnitude. Say that it costs \$1 million to remove the first 90% of a pollutant. It would cost another million to remove the next 9%, another million to remove the next 0.9%, another million to get out the next 0.09%, and so on. And you'd never get to 0%.

There is still another reason that zero discharge is impractical. Everything's got to go somewhere. Pollutants removed from the water must be discharged into the air or dumped onto the land. There is no other place for them to go. We have run out of "aways"—that magical place where things used to be thrown when we were through with them.

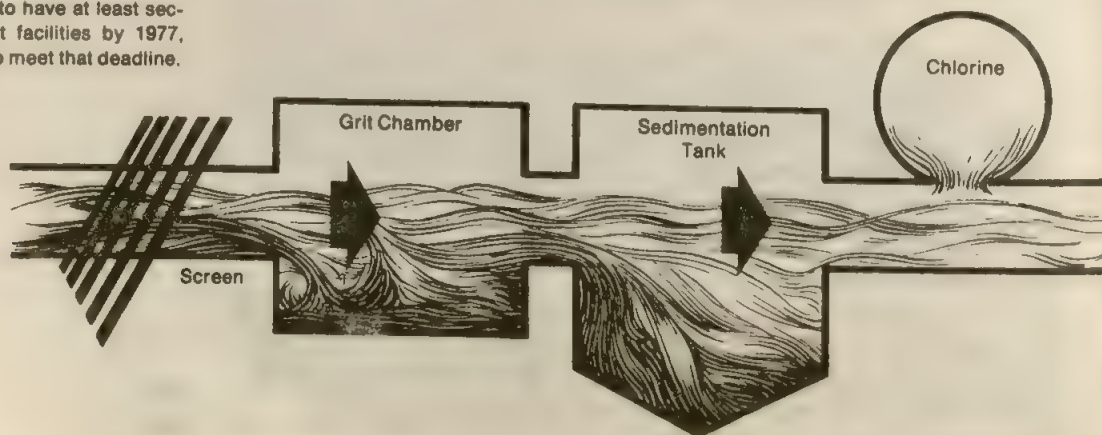
Wastewater-Treatment Plants

Most communities have *primary* sewage plants. This type of plant has holding tanks or ponds where the sewage is allowed to settle for a while (figure 18.12). This removes some of the solids as sludge. The primary step involves a very large BOD. Often, all the dissolved oxygen in the pond is used up and anaerobic decomposition—with its resulting odors—takes over. Effluent from a primary treatment plant contains a lot of dissolved and suspended organic matter, including pathogenic bacteria.

A *secondary* treatment plant passes the effluent from the primary treatment through sand and gravel filters. There is some aeration in this step, and aerobic bacteria convert most of the organic matter to stable inorganic materials.

A combination of primary and secondary treatment methods, known as the *activated sludge method* (figure 18.13), is quite commonly employed. The sewage is

Figure 18.12 A diagram of a primary treatment plant. All United States municipalities were to have at least secondary treatment facilities by 1977, but many failed to meet that deadline.



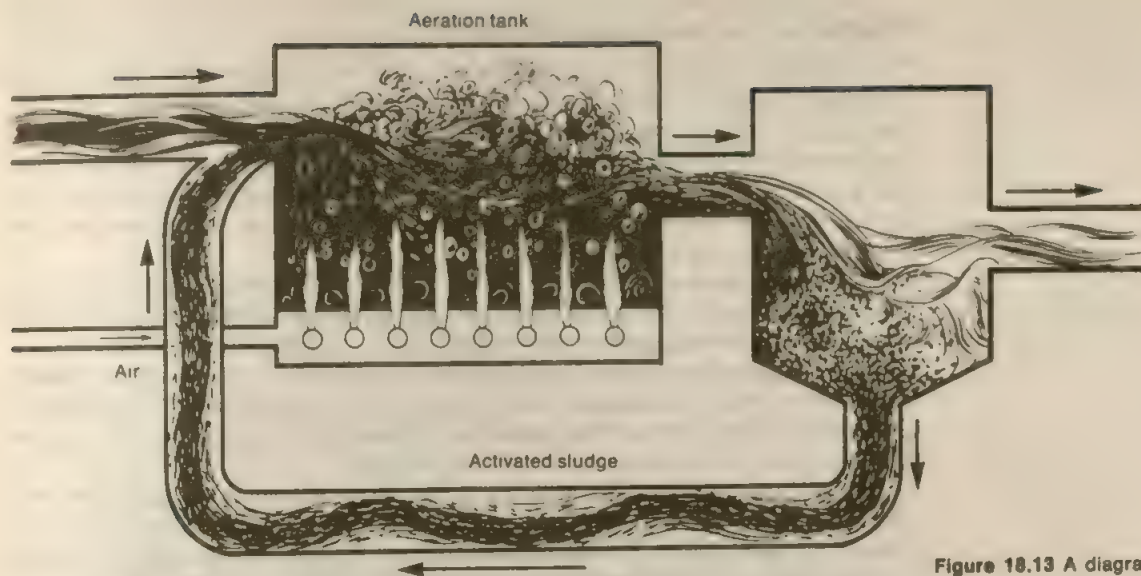


Figure 18.13 A diagram of a secondary treatment plant that uses the activated sludge method.

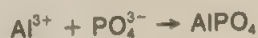
placed in tanks and aerated with large blowers. This causes the formation of large, porous clumps called *flocs*. These serve to filter and absorb contaminants. The aerobic bacteria further convert the organic material to sludge.

The effluent from sewage plants usually is treated with chlorine before it is returned to the waterway. Chlorine is added in an attempt to kill any pathogenic microorganisms that might remain. The effectiveness of chlorination has been questioned. Viruses, such as those that cause hepatitis, hardly seem to be effected. Further, chlorination is now thought to convert dissolved organic molecules into chlorinated hydrocarbons. Many chlorinated hydrocarbons, including such known carcinogens as chloroform (CHCl_3) and carbon tetrachloride (CCl_4), have been found in the drinking water of several cities that take their water from rivers. The concentration of these materials is in the parts-per-billion range. The threat they pose is probably small, but it's worrisome, nonetheless.

By the end of this century, even secondary treatment may be inadequate. Indeed, in some areas, it is already insufficient. Advanced, or *tertiary*, treatment will become increasingly important.

A number of new, experimental tertiary processes are being investigated. One type of tertiary treatment, using a multimedia filter, was put into operation in Lake Tahoe, California, in 1965. Charcoal filtration promises to become increasingly important, because charcoal adsorbs organic molecules that are difficult to remove by any other method.

Tertiary treatments often are designed to remove phosphates and nitrates. Partial phosphate removal is relatively easy. Aluminum ions from alum [$\text{Al}_2(\text{SO}_4)_3$] precipitate phosphate ions as insoluble aluminum phosphate.



Microorganisms and higher plants also have been used, with some success, for removal of phosphates. Nitrate removal is more difficult. Costly processes, such as reverse osmosis (pressure filtration through a semipermeable membrane), may be needed in some cases. Finding the money to finance adequate sewage treatment will be one of the major political problems for years to come.

Back to the Soil: An Alternative Solution

A consideration of an ecological cycle like that in **figure 18.8** leads to an alternative suggestion for the solution of our water-pollution problems. It seems absurd that we dump our sewage into our waterways. We deplete the land and foul the water in one step. Why not return the nutrients to the soil? In many societies, this has always been done: human and animal wastes have been returned to the soil. It is only in the "overdeveloped" countries that these vital resources are dumped into the waterways on a large scale.

Primitive people are usually very much a part of their natural world. We can even draw a simple ecological cycle for *Homo sapiens* (**figure 18.14**). Humans produce carbon dioxide and organic wastes. Plants use carbon dioxide and nutrients from the bacterial breakdown of organic wastes to produce food and oxygen. People consume the food and oxygen, and the cycle (much oversimplified here) is complete. It is only with the coming of the agricultural revolution that people began to live in cities and dump their wastes into the nearest streams.

Several pilot projects have been run on the return of activated sludge to the soil. The sludge could be dried, sterilized, and transported to farmlands. The chief problem is the high cost of transporting the sludge. This has been partially overcome by piping the suspended sludge directly to the fields. The water in the mixture serves to irrigate the crops; the sludge is a source of nutrients and humus.

A Swedish inventor, Rikard Lindström, has developed a toilet that composts wastes. It uses no energy or water. The mild heat of composting drives off water from the wastes. The system is ventilated to keep the process aerobic. No odors enter the house from a properly installed system. Dried waste is removed once a year or so. The Clivus-Multrum Company of Sweden markets the device and has licensed companies in the United States to make and sell the units. The only drawback is the system's initial cost—\$1,000 or more.

Other companies are working on systems that dispose of human wastes without dumping them into our waterways (see reference 11 for examples). We can't ever go back to the simple ways of our primitive ancestors, but we can act more in accord with the laws of nature.

A Drop to Drink

The water we drink usually comes from reservoirs, lakes, and rivers. A number of cities use water that has been used by other cities upstream. Such water may be

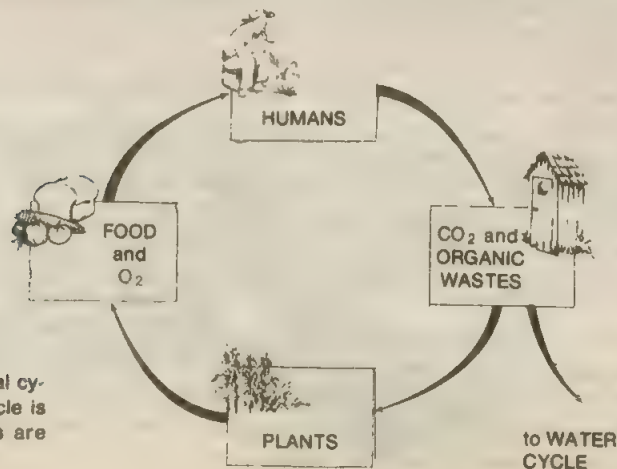


Figure 18.14 A simple ecological cycle for primitive people. The cycle is disrupted when human wastes are dumped into the waterways.

badly polluted with chemicals and pathogenic microorganisms. To make it safe and palatable involves several steps of chemical and physical treatment (**figure 18.15**).

The water to be purified usually is placed in a settling basin, where it is treated with slaked lime and a flocculant such as aluminum sulfate. These materials react chemically to form a gelatinous mass, aluminum hydroxide.



Slaked
lime

Aluminum
sulfate

Aluminum
hydroxide

Calcium
sulfate

The aluminum hydroxide carries down dirt particles and bacteria. The water then is filtered through sand and gravel. Sometimes water is sprayed into the air to remove odors and improve its taste (water without dissolved air tastes flat). Sometimes the water is filtered through charcoal to remove colored and odorous compounds. In the final step, chlorine is added to kill any remaining bacteria. In some communities using river water, a lot of chlorine is needed to kill all the bacteria, and you can taste the chlorine in the water.

As in the wastewater treatment, chlorination can produce toxic chlorinated compounds when organic substances are present in the water. To avoid this hazard, ozone sometimes is used to disinfect drinking water. Many European cities, including Paris and Moscow, use ozone to treat their drinking water. Ozone is more expensive than chlorine, but less of it is needed. An added advantage is that ozone kills viruses on which chlorine has little effect. Tests in Russia have shown ozone to be 100 times more effective than chlorine for killing polio viruses.

Ozone (O_3) acts by transferring its extra oxygen to the contaminant. The oxidized contaminants are thought to be less toxic than the chlorinated ones. In addition, ozone imparts no chemical taste to the water. We may well see a shift from chlorine to ozone in the treatment of our drinking water and wastewater.

We generally take our drinking water for granted. Perhaps we shouldn't. There are at least 4000 cases of water-borne illnesses in the United States each year, and perhaps 10 times as many. Twenty million people have no running water at all, and many of these people get water from suspect sources. Another 30 million tap individual wells or springs. Many of these sources are of uncontrolled and unknown

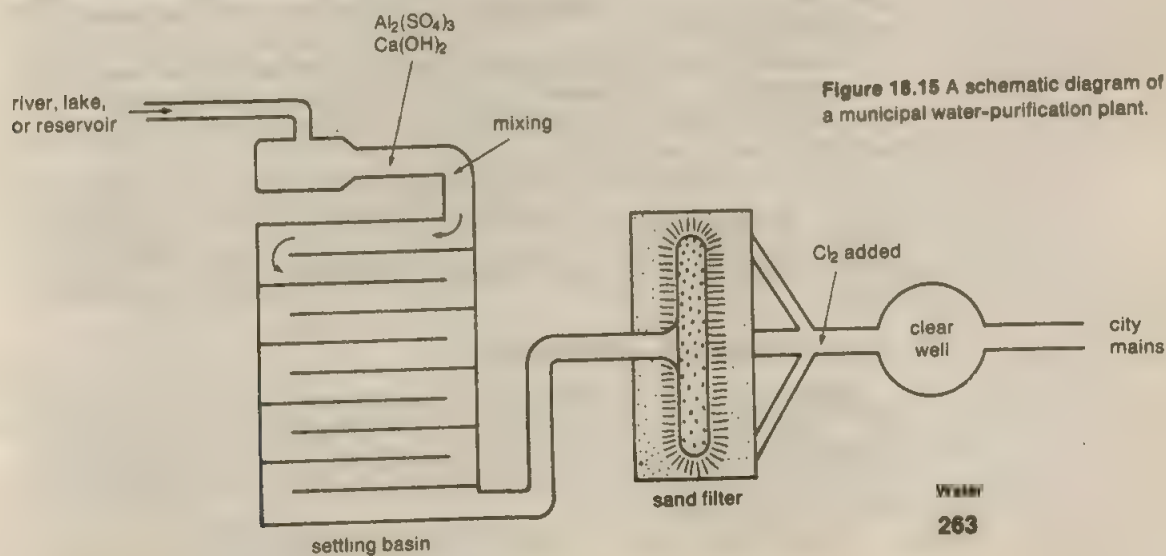


Figure 18.15 A schematic diagram of a municipal water-purification plant.

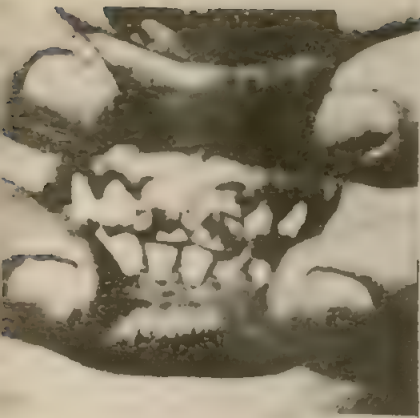


Figure 18.16 Excessive fluoride consumption can cause mottling of tooth enamel. (Courtesy of the National Institute of Health, Washington, D.C.)

quality. Much remains to be done before we can all be assured of safe drinking water.

Poison in the Drinking Water: Fluorides

Many communities add some form of fluoride salt to the municipal water supply. Fluoride salts, in moderate to high concentrations, are acute poisons. Indeed, sodium fluoride (NaF) is used as a poison against such pests as roaches and rats. Small amounts of fluoride ion, however, are essential for our well-being. Up to a point, the hardness of our tooth enamel can be correlated with the amount of fluoride present in our bodies. Concentrations of 0.7 to 1.0 ppm, by weight, of fluoride (usually as H_2SiF_6 or Na_2SiF_6) have been added to the drinking water of many communities for years. Evidence indicates that such fluoridation results in a reduction in the incidence of dental caries (cavities) by as much as 50% in some areas. Interpretation of the statistics is complicated, however, by the varying occurrence of fluorides in the diet and by the fact that individuals retain fluorides at remarkably different rates. One thing that you don't have to worry about is acute poisoning from fluoridated drinking water. You would have to drink 4000 L of water containing 1.0 ppm of fluoride to approach the lethal dose of 4 g. And that 4000 L would have to be consumed in a fairly short period of time.

There is some concern about the cumulative effect of consuming fluorides in drinking water, in the diet, in toothpastes, and from other sources. Excessive fluoride consumption can cause mottling of the tooth enamel. The enamel becomes brittle in certain areas and gradually becomes discolored. Fluorides also interfere with calcium metabolism, with kidney action, with thyroid function, and with the action of other glands and organs. The fluoridation of public water supplies probably will remain a subject of controversy for some time.

Poison in the Drinking Water: Nitrates

Some communities, usually the smaller ones, and many individual families obtain water from wells. There's even trouble with well water. The water table is dropping in most parts of the country, thus ever deeper wells are required. And even the groundwater is contaminated. In many agricultural areas, the concentration of nitrates (NO_3^-) in well water is above the maximum safe level (for infants) of 10 ppm. For adults, the maximum safe level is set at 50 ppm. Even this level is being approached in some areas.

Excessive nitrates (which are reduced to nitrites in the digestive tract) cause methemoglobinemia, the blue baby syndrome. In parts of Illinois, baby pigs turn blue and die after drinking the water. In California's Imperial Valley, some parents have to buy bottled water for their babies.

Nitrates in the groundwater come from agricultural fertilizers, from decomposition of organic wastes in sewage treatment, and from runoff from animal feedlots. Nitrates are highly soluble and so are difficult to remove from water. Only an expensive tertiary treatment can remove these compounds from water once they are there.

You're the Solution to Water Pollution

Congress has passed laws requiring that industries and municipalities stop discharging pollutants into our waterways. These laws probably will call a halt to the pollution of water by industry. Even though the laws call for an end to pollution by municipal sewage-treatment facilities, too, the end to this facet of water pollution seems to be less certain.

As population pressure increases, we must build bigger, better, and more costly

sewage-treatment plants. You, the citizen, must foot the bill for the disposal of your wastes. Just to maintain the present (largely inadequate) water quality will cost plenty. To clean our water up and then keep it clean will cost even more. The cost of unclean water is even higher—discomfort, loss of recreation, illness, even death.

In the long run, we must curb our population's growth. But the people are here—now. And the population will increase for several decades even if the birthrate stays at the "replacement" level of two children per family.

What can you do? You can demand enforcement of laws to bring an end to water pollution by industries and municipalities. And you can be ready to pay the price. You can persuade your neighbors that they also must pay the price. And you can stop wasting water. We must use the waters of the Earth as though they were all we had—because they are.

Problems

1. Describe primary and secondary sewage treatment. What does each process remove? What remains in the water after effective secondary treatment?
2. Describe briefly two methods of tertiary water treatment. What does each method remove?
3. What is the role of aerobic oxidation in sewage treatment?
4. What is anaerobic degradation? Why would it be undesirable in a sewage-treatment process?
5. What is methemoglobinemia? How is it caused?
6. We might increase our supply of fresh water by desalinating sea water. Read about the desalination process in reference 15 or in other sources and prepare a brief report on desalination by one or more of the following methods.
 - a. distillation
 - b. freezing
 - c. membrane separation (reverse osmosis)
 - d. electrodialysis
 - e. ion exchange
7. What impurities are present in groundwater?
8. What impurities are present in rainwater?
9. What is hard water? Why is it undesirable?
10. What is distilled water? Is it totally pure?
11. Can we ever achieve "zero" pollution? Why or why not?
12. Should human wastes be returned to the soil? Why or why not?
13. What is BOD? Why is a high BOD undesirable?
14. What type of sewage-treatment plant does your community have? Is it adequate? What chemicals (if any) are added during the treatment process?
15. What is the source of your community's water supply? Is it always adequate? Is it safe?
16. What is the nitrate content of the water you drink?
17. How much chlorine does your municipality add to the water you drink?
18. Is the water you drink fluoridated? Why or why not?
19. Drainage from coal mines adds 7 million t of sulfuric acid (H_2SO_4) to our waterways each year. How much lime (CaO) would it take to neutralize this acid, assuming complete reaction? The equation is:



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chapter 19

Air: Breath of Life... Or Death?

Without food, we could live about a month. Without water, we could live a few days. But, without air, we would die in minutes. We may run short of food, and we may run short of clean, fresh water, but we aren't likely to run out of air. What we may do is foul the air so that we become sick from it and some of us die prematurely. In some localities, the air eventually may get so bad that a lot of people will die.

It won't happen, you say? Certainly, we all hope that it won't. But we had better do more than hope. Read on!

Doomsday in Donora

The scene is a small industrial town at the bottom of a river valley. The time is late October. A dense smog settles over the valley. The air is acrid with sulfur dioxide. Dust (probably fly ash) settles over the land in a layer so thick that footprints and tire tracks are visible in it. A Halloween parade passes through the streets, with the marchers holding handkerchiefs over their faces in an attempt to keep the smog out of their lungs. People become seriously ill. Before the smog lifts 5 days later, 17 people are dead. Four more, who became ill in October, die by Christmas Eve. Nearly half the population is made ill by the smog. One in 10 is seriously ill.

What is this? A scene from a futuristic, nightmarish science fiction story? No! It is history. The scene actually took place in Donora, Pennsylvania, in 1948. A zinc-manufacturing plant and a huge iron and steel mill contributed to the smog. So did trains, automobiles, and even barges on the Monongahela River. An atmospheric inversion—a still, warm upper layer of air preventing the cooler lower layers from rising—kept the smog socked in on the valley (figure 19.1).

Is Donora a preview of what is in store for us all? Doomsday, U.S.A.? Before we attempt to prophesy, let's look at what air is and how it is polluted.

The Air Our Ancestors Breathed

Even before there were people there were cases of air pollution. Volcanoes

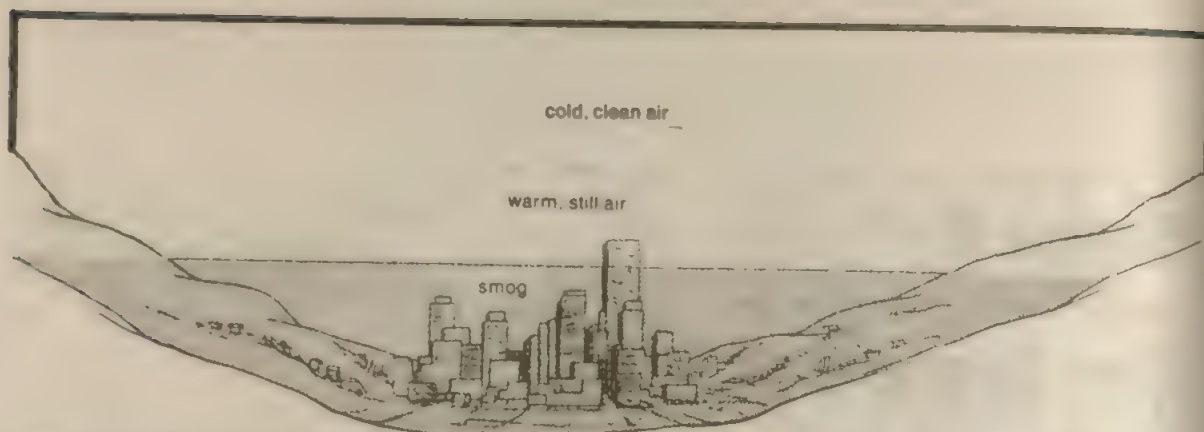


Figure 19.1 An atmospheric inversion traps smog in a valley.

erupted, spewing ash and poisonous gases into the atmosphere. There were dust storms. Gases collected over marshes. When people appeared on the scene and began their conquest of nature, they also began to pollute the air. They built fires that filled the air with smoke. They cleared land; this made possible even larger dust storms. They built cities, and the soot from their hearths and the stench from their wastes filled the air. The Roman author Seneca wrote in A.D. 61 of the "stink," soot, and "heavy air" of the imperial city. In 1257, the queen of England was forced to move away from the city of Nottingham because the heavy smoke was unendurable. The industrial revolution brought even worse air pollution. Coal was burned to power the factories as well as to heat the homes. Soot, smoke, and sulfur dioxide filled the air. The good old days? Not in the factory towns. But there were large rural areas relatively unaffected by air pollution.

Pollution Goes Global

With the increasing population, the whole world is becoming more urban. It is the huge megalopolises that are most afflicted by air pollution. But rural areas are not unaffected. In the neighborhoods around smoky factories, there is evidence of increased rates of spontaneous abortion and of poor wool quality in sheep, decreased egg production and high mortality in chickens, and increased feed and care required for cattle. Plants are stunted, deformed, and even killed. The giant Ponderosa pines are dying over a hundred miles from the smog-plagued Los Angeles basin. Orbiting astronauts visually traced drifting blobs of Los Angeles smog as far east as western Colorado. Other astronauts, over 100 km up, were able to see the plume of smoke from the Four Corners power plant near Farmington, New Mexico. This was the only evidence that they could see from that distance that the Earth is inhabited!

Snow in Norway is discolored by pollutants from England and Germany. Traffic police in Tokyo have had to wear gas masks and take "oxygen breaks"—breathing occasionally from tanks of oxygen. Buenos Aires, Sydney, Rome, Tehran, Ankara, Mexico City, and most of the cities of the world have had frightening episodes of air pollution.

The main difference between the air-pollution problem today and the problem in the past is that it is difficult to get away from air pollution now. The problem is worldwide. The air does purify itself, but we are pouring more pollutants into it than it can handle.



Figure 19.2 A cloud of volcanic ash from the eruption of Cerro Negro Volcano near León, Nicaragua in 1968. [Courtesy of the U.S. Geological Survey, Denver. Photo by W.L. Newman.]

A Thin Layer of Air

We saw in chapter 9 that the atmosphere is a thin layer of gases that extends only a few kilometres above the surface of the Earth. It is a mixture principally of nitrogen (N_2 , 78%), oxygen (O_2 , 21%), and argon (Ar, 1%). Water vapor and carbon dioxide are other important constituents of natural air.

What is a pollutant? It's merely a chemical in the wrong place in the wrong concentration. For example, ozone is a natural and important constituent of the upper atmosphere, where it serves to shield the Earth from life-destroying ultraviolet radiation. In the lower atmosphere, however, ozone is a dangerous pollutant, as we will see.

Coal + Fire → London Smog

There are two basic types of smog. One type, which consists mainly of smoke, fog, sulfur dioxide, sulfatic acid (H_2SO_4), ash, and soot is called *London smog*. Indeed, the word *smog* is thought to have originated in England in 1905 as a contraction of the words *smoke* and *fog*.

Probably the most notorious case of smog in history settled over London on Thursday, 4 December 1952. A large cold air mass moved into the valley of the Thames River. A temperature inversion placed a blanket of warm air over the cold air. With nightfall, a dense fog and below-freezing temperatures caused the people of London to heap coal into their small stoves. Millions of these fires burned through the night, pouring sulfur dioxide and smoke into the air. The next day (Friday), the people continued to burn coal when the temperature remained below freezing. The factories added their smoke and chemical fumes to the atmosphere.

Saturday was a day of darkness. For 20 miles around London no light came through the smog. The air was cold and still. And the coal fires continued to burn throughout the weekend.

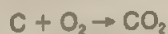
On Monday, 8 December, more than 100 people died of heart attacks while desperately trying to breathe. People tried to sleep sitting up in chairs in order to breathe a little easier. The city's hospitals were overflowing with people with respiratory diseases.

By the time a breeze cleared the air on Tuesday, 9 December, more than 4000 deaths had been attributed to the smog. Other people afflicted at the time died later. The total death count has been estimated at 8000.

The smog at Donora was essentially London smog, with a few added ingredients—chlorides, fluorides, arsenic, lead, and zinc.

The Chemistry of London Smog

The chemistry of London smog is fairly simple. Coal is mainly carbon, but it contains as much as 3% sulfur. Coal also contains varying amounts of mineral matter. When burned, the carbon in coal is oxidized to carbon dioxide.



Heat is given off in this process. Not all the carbon is completely oxidized. Some of it winds up as carbon monoxide.



Still other carbon, essentially unburned, ends up as soot.

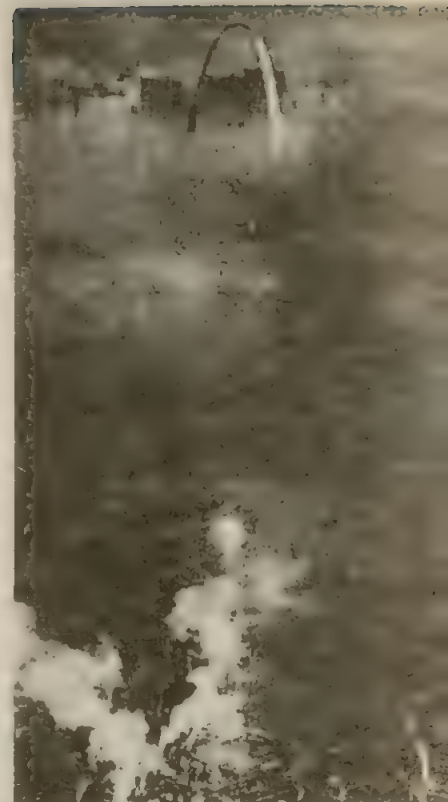
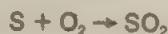


Figure 19.3 St. Louis' Gateway to the West Arch rises above a gloomy layer of smog. (Robert C. Holt, Jr., *St. Louis Dispatch*.)



Figure 19.4 London smog is often highly visible, with soot and fly ash forming a dark pall of smoke. (Courtesy of Henry H. Valiukas, Minnesota Environmental Control Citizens Association, St. Paul.)

The sulfur in coal also burns. It forms a choking acid gas called sulfur dioxide.



Sulfur dioxide is readily absorbed in the respiratory system. It is a powerful irritant. Sulfur dioxide is known to aggravate the symptoms of people who suffer from asthma, bronchitis, emphysema, and other lung diseases.

As if sulfur dioxide were not bad enough, things get worse. Some of the sulfur dioxide reacts further with oxygen in the air to form sulfur trioxide.



The sulfur trioxide then reacts with water to form sulfuric acid.

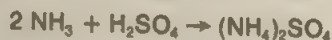


Sulfuric acid is even more irritating to the respiratory tract than is sulfur dioxide.

Usually, London smog also is characterized by high levels of *particulate matter*, solid and liquid particles of greater than molecular size. The larger particles often are visible in the air as dust and smoke. Smaller particles of $1 \mu\text{m}$ or less in diameter are called *aerosols*. These are often invisible.

Particulate matter consists in part of soot (unburned carbon). A larger portion is made up of the mineral matter that occurs in coal. These minerals do not burn. Some are left behind as *clinkers*. In the roaring fire of a huge factory or power plant, however, much of this solid material is carried aloft in the tremendous draft. This *fly ash* settles over the surrounding area, covering everything with dust. It is also inhaled, thus contributing to respiratory problems in animals and humans.

Perhaps a more insidious form of particulate matter is the sulfates. Some of the sulfuric acid in smog reacts with ammonia to form a solid material, ammonium sulfate.



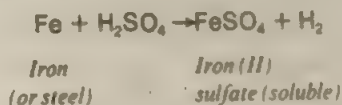
Sulfuric acid, in the form of minute liquid droplets, and the solid ammonium sulfate are easily trapped in the lungs. The harmful effect of these pollutants may be considerably magnified by their interaction. A certain level of sulfur dioxide, without the presence of particulate matter, might be reasonably safe. A certain level of particulate matter, without sulfur dioxide around, might be fairly harmless. But take the same levels of the two together, and the effect might well be deadly. The sort of interaction in which the total effect is much greater than that of either ingredient separately is called *synergism*. Synergistic effects are quite common whenever chemicals get together. We encounter synergism again in our study of the action of drugs (chapter 23).

Sulfur Oxides: Effects on People, Plants, Steel, and Stone

The oxides of sulfur and aerosol mists of sulfuric acid are damaging to plants, building materials, and people. The leaves of green plants become bleached and splotchy when exposed to sulfur oxides. The yields and the quality of farm crops can be severely affected.

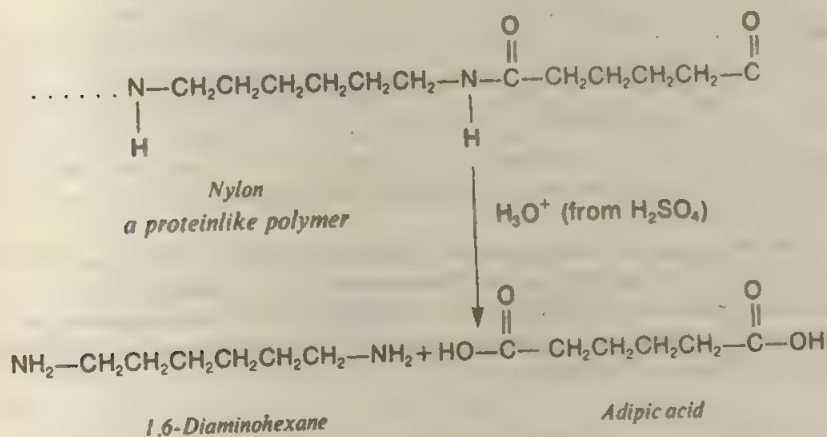
Rain in industrialized countries has become more acidic in recent years. This change has been attributed to the increased amounts of sulfur oxides being released into the atmosphere. Acidic rainwater can corrode metals, eat holes in nylon hose, and even decompose stone buildings and statues.

Sulfuric acid eats away metal to form a soluble salt and hydrogen gas.



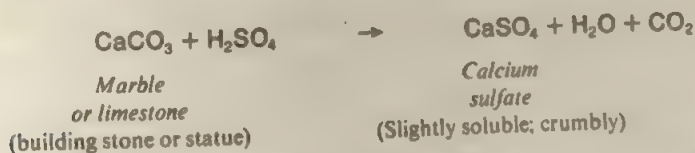
The reaction shown here is oversimplified. For example, in the presence of oxygen (air), the iron is converted to rust (Fe_2O_3).

Nylon reacts with sulfuric acid; the polymer molecules are broken down and they revert to the diamine and diacid from which the nylon was made.



Thus, the long-chain molecules that form the fibers of the nylon hose are broken down and the stockings disintegrate.

Marble in buildings and statues is disintegrated by sulfuric acid in a similar reaction.



Perhaps even more serious than their effect on plants and building materials is the effect of sulfur oxides on people. When these pollutants come into contact with the alveoli of the lungs, the cells are broken down. The alveoli lose their resilience, making it difficult for them to expell carbon dioxide. Such lung damage leads to—or at least contributes to—pulmonary emphysema, a condition characterized by an increasing shortness of breath. Emphysema is the fastest growing cause of death in the United States. Most likely the principal factor in the rise of emphysema is cigarette smoking. However, air pollution is known to be a factor, too. For instance, the incidence of the disease among smokers is three times as great in St. Louis, where air pollution is rather heavy, as in Winnipeg, Manitoba, where air pollution is rather mild. The United States Environmental Protection Agency recently has expressed concern that catalytic converters, placed on automobiles to decrease the amount of certain pollutants, actually might lead to an increased concentration of sulfuric acid mists in urban areas. This would lead to increased risks to human health. The problem is still being studied.



Figure 19.5 This stone sculpture on the exterior of Herten Castle, near Recklinghausen in Westphalia, Germany, shows the effects of acidic smog. The castle was constructed in 1702. (a) The sculpture as it looked in 1908. (b) The sculpture as it looked in 1969. (Reprinted with permission from Winkler, E. M., *Stone: Properties, Durability in Man's Environment*, Berlin: Springer-Verlag, 1973. Copyright © 1973 by E. M. Winkler.)

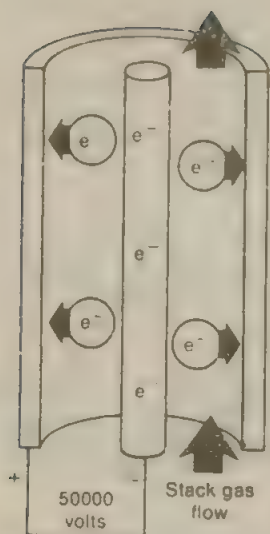


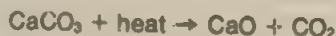
Figure 19.6 Cross section of a cylindrical electrostatic precipitator. Electrons from the negatively charged discharge electrode (in the center) attach themselves to the particles of fly ash and give them a negative charge. The charged particles then are attracted to the positively charged collector plate, on which they are deposited.

What to Do about London Smog

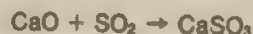
Much research has gone into the prevention and alleviation of London smog. Soot and fly ash can be removed effectively by electrostatic precipitators. These devices induce electrical charges on the particles, which then are attracted to oppositely charged plates and deposited (**figure 19.6**). You should remember, though, that you can't get something for nothing. Electrostatic precipitators use large amounts of electricity. That electrical energy has to come from somewhere. You also should remember that everything has got to go somewhere. Fly ash removed from the air has to be put on the land or in the water, although it could be used. Research engineers at the University of Illinois are working on ways to use fly ash in building materials.

The elimination of sulfur dioxide is more difficult. Low-sulfur coal is scarce and expensive. The most plentiful fuel we have is low-grade, high-sulfur coal. Pilot runs have shown that sulfur can be washed from finely pulverized coal, but the process is expensive. There are also processes for converting dirty coal to clean liquid and gaseous fuels. These methods involve the reduction of carbon to hydrocarbons (chapter 13). These processes may hold promise for the future, but they are too expensive to compete economically with other fuels at present. And they waste a part of the coal's energy.

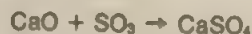
A third way to get rid of the sulfur is to scrub the sulfur dioxide out of the stack gases after the coal has been burned. Perhaps the most promising of the scrubbers is the limestone-dolomite process. Limestone (CaCO_3) and dolomite (a mixed calcium-magnesium carbonate) are pulverized and heated. Heat drives off carbon dioxide and a reactive basic oxide is left.



The basic oxide reacts with SO_2 and SO_3 to form solid calcium sulfite and calcium sulfate.



*Calcium
sulfite*



*Calcium
sulfate*

These solid by-products present a sizable solid-waste-disposal problem. Removal of 1 t of sulfur dioxide produces about 2 t of solids.

The sulfur dioxide may be reacted with hydrogen sulfide and recovered as elemental sulfur.



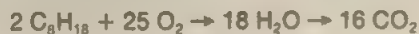
Los Angeles Smog

The other main type of smog is *Los Angeles smog*, or, more properly, *photochemical smog*. Unlike London smog, which accompanies cold, damp air, photochemical smog usually occurs during dry, sunny weather. The principal culprits are unburned hydrocarbons and oxides of nitrogen from automobiles. The warm, sunny climate that has drawn so many people to the Los Angeles area is also the perfect setting for photochemical smog.

The chemistry of Los Angeles smog is exceedingly complex. Let's look at the stuff that comes out of an automobile's exhaust pipe and examine the pollutants one at a time.

Carbon Monoxide: The Quiet Killer

When a hydrocarbon burns in sufficient oxygen, the products are carbon dioxide and water. Since both of these substances are normal constituents of air, they are not generally considered to be pollutants. Let's illustrate the combustion process with an octane, one of the hundreds of hydrocarbons that make up the mixture we call gasoline.



When insufficient oxygen is present, another oxide of carbon, carbon monoxide (CO), is formed. Millions of metric tons of this invisible but deadly gas are poured into the atmosphere each year, about 75% of it from automobile exhausts. The danger level for carbon monoxide is 10 ppm. Even in off-street urban areas, the level often averages 7 to 8 ppm. On the streets, the danger level is exceeded much of the time. Such levels do not cause immediate death, but, over a long period, exposure can cause impairment of physical and mental processes. Levels much higher than 10 ppm can be tolerated only for short periods of time.

Carbon monoxide is an invisible, odorless, tasteless gas. There is no way for a person to tell that it is around (without using test reagents or instruments). Drowsiness is usually the only symptom, and that is not an unpleasant one. How many auto accidents are caused by drowsiness or sleep induced by carbon monoxide? No one knows for sure. And you shouldn't smoke while you drive in heavy traffic. Cigarette smoke contains a fairly high concentration of carbon monoxide, and so you would get a double dose!

You won't necessarily escape carbon monoxide by going inside. The air inside office buildings, airport terminals, and apartments has been found to have essentially the same concentration of CO as the air outside them. In some areas, this level exceeds federal safety standards. It has been recommended that such buildings be tightly sealed at lower levels and that they be spaced in such a way that the wind can disperse the pollutants around them.

Carbon monoxide is not an irritant. It exerts its insidious effect by tying up the hemoglobin in the blood. The normal function of hemoglobin is to transport oxygen (figure 19.8). Carbon monoxide binds to hemoglobin so strongly that the hemoglobin is prevented from transporting oxygen. Therefore, the symptoms of CO poisoning are those of oxygen deprivation. All except the most severe cases of carbon monoxide poisoning are reversible. The best antidote is the administration of pure oxygen. Artificial respiration may help if a tank of oxygen is not available.

With carbon monoxide poisoning, the ability of the blood to transport oxygen is impaired, and the heart has to work harder to supply oxygen to the tissues. Chronic exposure to even low levels of CO may put an added strain on the heart, which may lead to an increased chance of a heart attack.

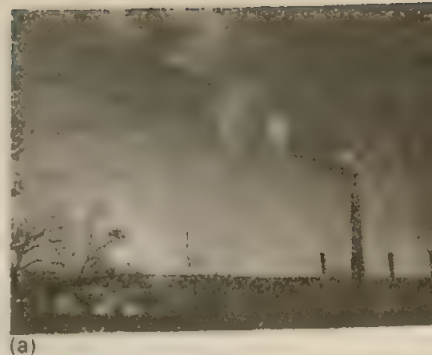


Figure 19.7 Northern States Power Company's High Bridge power plant in St. Paul. (a) Before the installation of an electrostatic precipitator. (b) After. (Courtesy of the Northern States Power Company.)

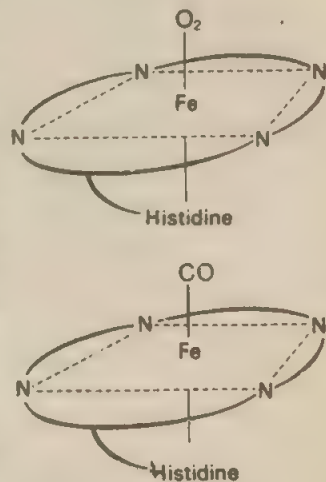


Figure 19.8 Schematic representations of a portion of the hemoglobin molecule. Histidine is an amino acid. Carbon monoxide bonds much more tightly than oxygen, as indicated by the heavier bond line.



Figure 19.9 Downtown Los Angeles on a smoggy day in 1956. Smog is trapped by a temperature inversion, with a layer of warm air only 100 m above the ground. The upper portion of Los Angeles City Hall can be seen in the clear air above the base of the inversion. (Courtesy of the Los Angeles County Air Pollution Control District.)



These oxygen atoms react with other components of automobile exhaust and the atmosphere to produce a variety of irritating and toxic chemicals (Figure 19.10).

At present concentrations, the oxides of nitrogen don't seem particularly dangerous in themselves. Nitric oxide at high concentrations reacts with hemoglobin, and, as with carbon monoxide poisoning, this leads to oxygen deprivation. Such high levels seldom, if ever, result from ordinary air pollution, but they might be reached in areas close to some industrial sources. Nitrogen dioxide is an irritant to the eyes and the respiratory system. Tests with laboratory animals indicate that chronic exposure to levels in the 10-25-ppm range might lead to emphysema and other degenerative diseases of the lungs.

The most serious environmental effect of the nitrogen oxides is that they produce smog. However, these gases also contribute to the fading and discoloration of fabrics. By forming nitric acid, nitrogen oxides contribute to the acidity of rainwater, accelerating the corrosion of metals. They also contribute to crop damage, although

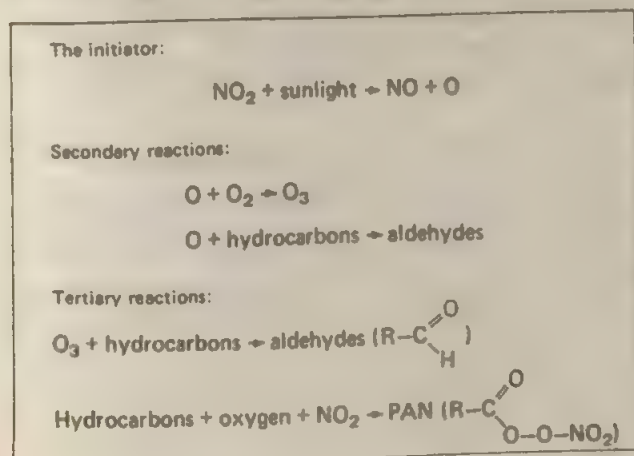


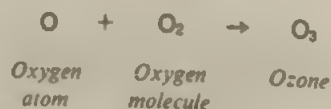
Figure 19.10 A summary of some of the principal reactions in the formation of photochemical smog. Most reactive intermediates have been omitted from this simplified scheme. (For a complete account, see reference 1.)

their specific effects are difficult to separate from those of sulfur dioxide and other pollutants.

Ozone: Good News, Bad News

Ozone is a natural component of the upper atmosphere. There it serves to shield the Earth from life-destroying ultraviolet radiation. Ozone is also a familiar constituent of photochemical smog. Inhaled, it is a toxic, dangerous chemical. Ozone is a good example of just what a pollutant is—a chemical substance out of place in the environment. In the upper atmosphere, it helps make life possible. In the lower atmosphere—the part that we breathe—it makes life difficult.

Ozone is formed by the reaction of oxygen atoms with oxygen molecules.



Recall that oxygen atoms are formed when sunlight splits nitrogen dioxide molecules.

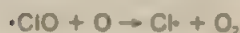


Ozone is a powerful oxidizing agent. At low levels, it causes eye irritation. At high levels, it can cause pulmonary edema, hemorrhage, and even death. The long-term effects of exposure to low levels of ozone are more difficult to evaluate. Inhalation of ozone is particularly dangerous during vigorous physical activity. Members of a New Jersey high school football team had to be hospitalized after collapsing during a severe pollution episode. School children in Los Angeles are not allowed to play outside when ozone reaches dangerous levels, as it often does. At concentrations as low as 0.15 ppm, ozone causes damage to vegetation within an hour. Exposure of animals to 1 ppm of O_3 for 8 hours a day for a year has produced in them bronchial inflammation and irritation of fibrous tissues. It is not known whether or not the same thing occurs in humans. It is known that ozone levels have occasionally reached 0.5 ppm in southern California. Levels of 0.15 ppm are exceeded frequently.

In addition to adversely affecting health, ozone causes economic damage. It causes rubber to harden and crack. This shortens the life of automobile tires and other rubber items. And, as was suggested in the preceding paragraph, ozone causes extensive damage to crops. Tobacco and tomatoes are particularly susceptible.

The Ozone Layer: Chlorofluorocarbons, the SST, and Nuclear Bombs

We encountered a class of compounds called chlorofluorocarbons in chapter 11. These compounds are quite useful as propellants in aerosol cans and as refrigerants. A controversy over their use arose in 1974. F. Sherwood Rowland, a chemist at the University of California at Irvine, considered the effect of these compounds on the Earth's protective ozone layer. He speculated that, because of their inertness to ordinary chemical reagents, chlorofluorocarbons might be making their way up through the atmosphere to the stratosphere. There, they may well react with atomic oxygen and ultraviolet light to form chlorine atoms, which catalyze the decomposition of ozone.



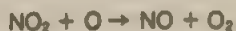
Note that the last step results in the formation of another chlorine atom that can break down another molecule of ozone. The second and third steps are repeated many times; thus, the decomposition of one molecule of chlorofluorocarbon can result in the destruction of many molecules of ozone.

The reactions noted here are known to occur in the laboratory under conditions simulating those in the stratosphere. In partial confirmation of Rowland's speculations, chlorofluorocarbons have been detected in the stratosphere. Their effect on the ozone layer has yet to be proven, but the risk involved is rather great. The National Academy of Sciences estimates that a 10% decrease in the thickness of the ozone layer would cause an increase of 8000 cases of skin cancer per year among the light-skinned population of the United States. Chlorofluorocarbons have been banned from use in most aerosol preparations.

There are other threats to the ozone layer. Several nations have built supersonic transport (SST) airplanes. To be economically feasible, these craft must cruise in the stratosphere. Some scientists are concerned that they might damage the ozone layer. As in other combustion processes, nitric oxide is produced by combustion in SST engines. The nitric oxide would deplete the ozone by converting it to ordinary oxygen.



The nitric oxide then is regenerated by the reaction of nitrogen dioxide with oxygen atoms.



The molecule of NO then can destroy another ozone molecule. The steps may be repeated many times; one nitric oxide molecule can destroy many ozone molecules.

Note that none of these processes has been demonstrated in the stratosphere. Damage to the ozone layer has not been shown. Some scientists worry, though, that by the time damage is demonstrated, it may be too late to do anything about it. We may seal our fate before any symptoms appear.

Hydrocarbons: Another Culprit

Hydrocarbons are released from a variety of natural sources. Of all those found in the atmosphere, only about 15% are put there by people. In urban areas, though, the processing and use of gasoline is the major source of hydrocarbons in the environment. Gasoline can evaporate anywhere along the line. This simple process contributes substantially to the total amount of hydrocarbons in urban air. The automobile's internal combustion engine also contributes by exhausting unburned and partially burned hydrocarbons.

Certain hydrocarbons, particularly those that contain a double bond, combine with oxygen atoms or ozone molecules to form aldehydes. Such reactions are very complicated, but they can be illustrated by the reaction of ethylene with atomic oxygen to form acetaldehyde.



Figure 19.11 F. Sherwood Rowland

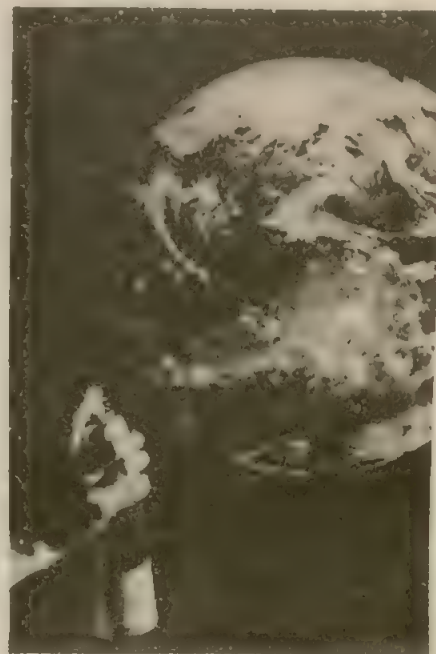
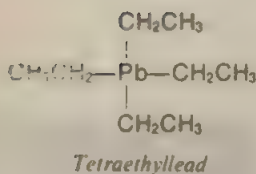
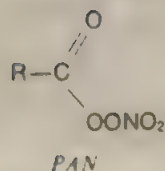
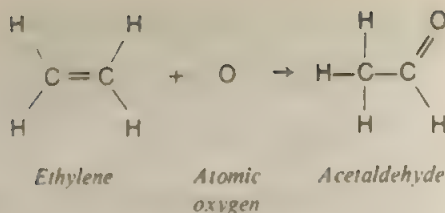


Figure 19.12 Is the ozone layer being destroyed by chlorofluorocarbon propellants? (Courtesy of the National Resources Defense Council, Inc., New York.)



Formaldehyde, the simplest of the aldehydes, also is formed, as are other more complicated aldehydes. As a class, the aldehydes have foul, irritating odors.

Another complicated series of reactions involving hydrocarbons, oxygen, and nitrogen dioxide leads to the formation of peroxyacynitrates (PAN).

Ozone, the aldehydes, and PAN are responsible for much of the destruction wrought by smog. They make breathing difficult and make the eyes smart and itch. Those who already have respiratory ailments may be severely afflicted. The very young and the very old are particularly vulnerable.

Get the Lead Out

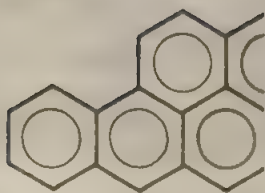
Lead (Pb), like mercury (Hg), is a heavy-metal poison that affects the functioning of the blood, the liver, the kidneys, and the brain. For years, a lead compound, tetraethyllead, has been used to improve the antiknock qualities of gasoline. Tetraethyllead is an extremely effective antiknock agent. As little as 0.5 to 1.0 g per litre (2 to 4 g per gallon) can raise the octane rating of gasoline by 10 or more units. It is also quite toxic. Gasoline that contains lead also must have a dye added to warn consumers of its presence.

Modern high-compression engines will not run on straight-run gasoline. As it comes from the distillation tower of a petroleum refinery, gasoline has an octane rating of about 60. Science and technology, through the use of tetraethyllead, have done a fine job of providing high-octane fuel. Unfortunately, the solution to one problem may be the source of another. Large amounts of lead have been spewed into the environment by automobiles. Fairly high concentrations of lead are now found along heavily traveled streets, freeways, and other roads.

Not everyone agrees that this lead at its present levels presents a health hazard. Surely, though, its continued use eventually would lead to dangerous concentrations in many areas. At any rate, there is now another problem with lead in gasoline. Lead fouls the catalysts in pollution-control devices. So there are two reasons we should "get the lead out."

To achieve the same octane rating in lead-free gasoline, more branched-chain and aromatic hydrocarbons (chapter 10) are needed. Even without these extra aromatics, the burning of gasoline produces 3,4-benzpyrene, a chemical that induces cancer in laboratory animals. Some scientists have warned that increasing the aromatic hydrocarbon content of gasoline would quite likely increase the concentration of this carcinogen in the atmosphere.

Catalytic converters and lead-free gasolines are far from perfect answers. Cars with pollution-control devices are harder to start and run less efficiently than cars without them. The catalyst in a converter speeds the further oxidation of carbon monoxide and hydrocarbons to carbon dioxide. When the engine is properly tuned, the catalytic converter does reduce the emission of these two pollutants. The catalyst used is often the precious metal platinum, which makes the converters rather expensive. Furthermore, the catalyst is not effective against nitrogen oxides. These pollutants can only be reduced by operating the engine at a lower temperature or with a lower air-to-fuel ratio. Unfortunately, these adjustments *increase* the amounts



3,4-Benzpyrene

of carbon monoxide and unburned hydrocarbons the engines produce. You just can't get something for nothing. Perhaps the answer in the long run will be the development of automobile engines that run on a lower octane fuel. Japan's Honda Motor Company has developed a stratified charge engine that not only runs on a lower octane fuel but meets the Environmental Protection Agency's emission standards as well. If we want clean air, we may have to settle for smaller, less powerful cars.

Who Pollutes? How Much?

Air pollution causes material damage by dirtying and destroying buildings, clothing, and other material objects. It increases health hazards, especially for the very young, the old, and those already ill. It causes crop damage by stunting or killing green plants. Air pollution reduces visibility, thus increasing auto and air traffic accidents. It is even an aesthetic problem, with its ugly smoke plumes and unpleasant odors.

Who causes all that pollution? **Table 19.1** lists estimates of sources in the United States for 1976. The table merely indicates the total weights of pollutants. It does not reflect the obvious fact that some pollutants are more harmful than others.

Table 19.1
Emissions of air pollutants in the United States by source, 1976

Source	Millions of Metric Tons	Percentage
Transportation	92.6	51.9
Fuel combustion in stationary sources (mainly power plants)	40.9	22.9
Industrial processes	28.3	15.9
Solid-waste disposal	4.1	2.3
Miscellaneous (mainly forest fires, agricultural burning, coal-waste fires, oil and gas production)	12.5	7.0
Total	178.4	100.0

Adapted from "National Air Quality and Emissions Trends Report, 1976," Research Triangle Park, N.C.: United States Environmental Protection Agency, 1977.

Looking at **table 19.1**, we can conclude that transportation accounts for most of the air pollution in the United States. Since most transportation in the United States is by private automobile, it is the family car that is doing the most toward doing us in.

Perhaps it would be more informative for us to look at the amount of each of the major air contaminants produced in the United States each year. These estimates are given in **table 19.2**. Quantitatively, carbon monoxide is obviously the major pollutant. Mainly on the basis of anticipated carbon monoxide levels, the Environmental Protection Agency has called for gas rationing in Los Angeles and traffic restrictions in several other cities.

Table 19.2
Emissions of major air pollutants in the United States, 1976

<i>Pollutant</i>	<i>Millions of Metric Tons</i>	<i>Percentage</i>
Carbon monoxide	87.2	48.9
Hydrocarbons	27.9	15.6
Sulfur oxides	26.9	15.1
Particulate matter	13.4	7.5
Nitrogen oxides	23.0	12.9
Total	178.4	100.0

Adapted from "National Air Quality and Emissions Trends Report, 1976," Research Triangle Park, N.C.: United States Environmental Protection Agency, 1977.

Let's continue to pin down those polluters. **Table 19.3** shows the sources of carbon monoxide. We see that 80% of all carbon monoxide comes from transportation. The major culprit? Again, the private automobile.

Table 19.3
Emissions of carbon monoxide in the United States, 1976

<i>Source</i>	<i>Millions of Metric Tons</i>	<i>Percentage</i>
Transportation	69.7	79.9
Stationary sources	1.2	1.4
Industrial processes	7.8	9.0
Solid-waste disposal	2.8	3.2
Miscellaneous	5.7	6.5
Total	87.2	100.0

Adapted from "National Air Quality and Emissions Trends Report, 1976," Research Triangle Park, N.C.: United States Environmental Protection Agency, 1977.

Most hydrocarbons also are released from sources associated with transportation. Nitrogen oxides are produced mainly by gasoline-burning vehicles, with power plants a close second. Particulate matter comes mainly from industry.

What is the worst pollutant? Deciding that question involves a value judgment. Carbon monoxide is produced in huge quantities and is quite toxic. Yet the World Health Organization (WHO) rates sulfur oxides as the worst of all. Sulfur oxides are powerful irritants. According to WHO, people with respiratory illnesses are more likely to die from exposure to sulfur oxides than from exposure to any other kind of pollutant.

Where do the sulfur oxides come from? Here we find a different culprit (**table 19.4**). Fossil-fuel-burning power plants produce over 80% of all the sulfur oxides released into the atmosphere. But who uses electricity? You do. A 100-w bulb, burning for 1 year, uses electricity generated by burning 275 kg of coal.

Table 19.4
Emissions of sulfur oxides in the United States, 1976

<i>Source</i>	<i>Millions of Metric Tons</i>	<i>Percentage</i>
Transportation	0.8	3.0
Stationary sources	21.9	81.4
Industrial processes	4.1	15.2
Solid-waste disposal	0.0	0.0
Miscellaneous	0.1	0.4
Total	26.9	100.0

Adapted from "National Air Quality and Emissions Trends Report, 1976," Research Triangle Park, N.C.: United States Environmental Protection Agency, 1977

Who pollutes? We all do. In the words of the late Walt Kelly's comic-strip character Pogo, "We have met the enemy, and he is us."

What to Do about Air Pollution

Don't expect any easy solutions to our air-pollution problems. Neither industry nor government (alone or together) can solve the problem. As long as each of us has to have a huge automobile to drive to class or to the office or to run an errand, we will have a serious air-pollution problem. Automobiles contribute half of the total air pollution. Who drives automobiles? You do! If you really want to do something about air pollution, you can walk. Riding a bicycle is great for distances that are a little too far for walking. Use mass transit whenever possible. For comparable amounts of pollutants, buses and trains transport a lot more people. If you must use an automobile, form a car pool. Buy a smaller car with low emissions and without a lot of gadgetry.

You also can conserve electricity. Many utilities now offer helpful suggestions for saving electricity (and money!). This is certainly a hopeful sign. A few years ago electric power companies were urging us to use more electricity. Things are changing—for the better.

Air quality is getting better, also. Between 1970 and 1975, sulfur oxide emissions were reduced 25% and particulate matter 14%, with the largest gains in urban areas. Carbon monoxide levels are down in most cities. The levels of nitrogen oxides and oxidants are down in California. The air is still polluted at unsafe levels for much of the population at certain times, however, and smog is steadily encroaching on new areas. We still have a long way to go before we all have clean air to breathe, but perhaps we have at last turned the corner.

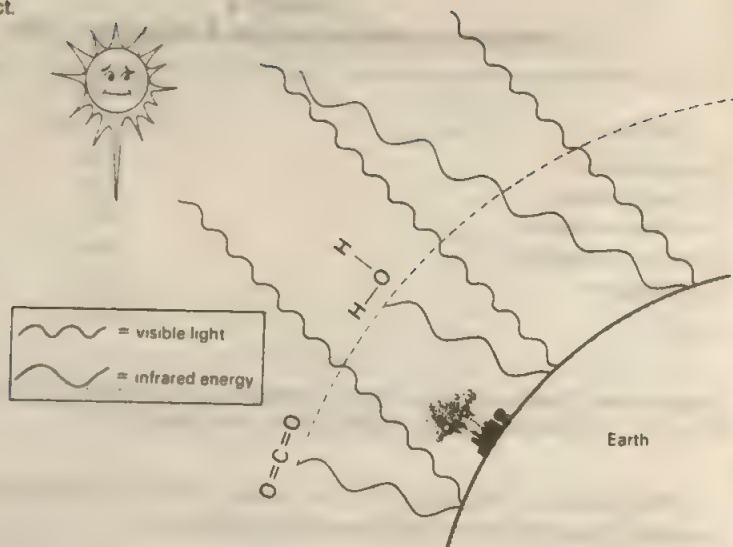
The Penultimate Pollutants: Carbon Dioxide and Water

No matter how clean an engine or a factory is, as long as it burns coal or petroleum products, it produces carbon dioxide and water. The concentration of carbon dioxide in the atmosphere has increased 7.5% in this century. It continues to increase at an expanding rate through the increased burning of carbon fuels.

We generally don't even consider carbon dioxide and water vapor to be pollutants. Both are natural components of the environment. Certainly their immediate effect upon us is slight. But what about their long-term effects?

Both water vapor and carbon dioxide produce the *greenhouse effect*. These chemicals let the sun's rays (visible light) in to warm the surface of the Earth, but,

Figure 19.13 The greenhouse effect.



when the Earth tries to radiate this heat (infrared energy) back out into space, the energy is trapped by the water and carbon dioxide molecules (figure 19.13). Water vapor spewed into the atmosphere soon falls back to Earth as rain. Therefore, it affects the climate mostly at the local level. Carbon dioxide, poured into the air, is not so readily dissipated. It hangs around to affect the climate of the entire world. The concentration of carbon dioxide is now increasing at a rate of 1 ppm per year. Some scientists predict a warming trend that will melt the polar ice caps, and flood coastal cities.

At present, the Earth's atmosphere seems to be cooling, not warming. We also pour soot, smoke, and dust into the atmosphere. These, perhaps aided by the vapor trails of jet aircraft, screen out the sun's light and tend to lower the Earth's temperature. We may not always be so lucky as to balance one effect against the other.

The Ultimate Pollutant: Heat

Electric cars were once strongly advocated as a solution to air pollution. But electric cars require electric power. Electric power requires power plants. Conventional power plants burn coal, gas, and oil. Replacing cars run on fossil fuel with ones run on electricity would serve only to change the *site* of the pollution and perhaps spread it out a bit.

Remember that there are losses at every step in the conversion and transmission of energy. More fossil fuels would have to be burned at power plants to provide the same amount of energy for propelling automobiles that we now use.

Nuclear power plants (chapter 13) have been proposed as pollution-free sources of energy. True, they do not spew soot, smoke, and poisonous chemicals into the atmosphere. But they do introduce some radioactivity into the environment, and there is still no effective way to dispose of radioactive wastes. And nuclear power plants dump vast quantities of residual heat into the environment. This heat may be the ultimate pollutant.

We use fantastic amounts of energy—in cars, factories, homes, schools, hospitals—use it everywhere and for everything. The release of energy heats up the environment. Eventually, this heat will change the climate of the Earth, and the ecology of the whole planet will be affected.

As Rene Dubos, world-renowned biologist, put it: "We will destroy our lives by producing more useless, destructive energy to make more and more needless things that do not increase the happiness of people."

Paying the Price

It has been estimated that air pollution costs the United States \$16 billion each year. It wrecks our health by causing or aggravating bronchitis, asthma, emphysema, and lung cancer. It destroys our crops and sickens and kills our livestock. It corrodes our machines, blights our buildings, and even destroys our works of art (figure 19.14).

Elimination of air pollution would not be cheap or easy. It is especially expensive to remove the last fractions of pollutants. Figure 19.15 shows how costs increase as you try to remove larger percentages of pollutants. Notice that the curves are exponential (chapter 15); costs soar to infinity as pollutants are reduced to zero. But we could have cleaner air. How clean depends on how much we are willing to pay.

What would we gain by getting rid of air pollution? How much is it worth to see the clear blue sky or to see the stars at night? How much is it worth to breathe clean, fresh air?

It would take a massive effort that included every individual, every industrial firm, and every unit of government on Earth. It would require informed, active citizens. Will we do this job? We must. It means preserving the very air we breathe.

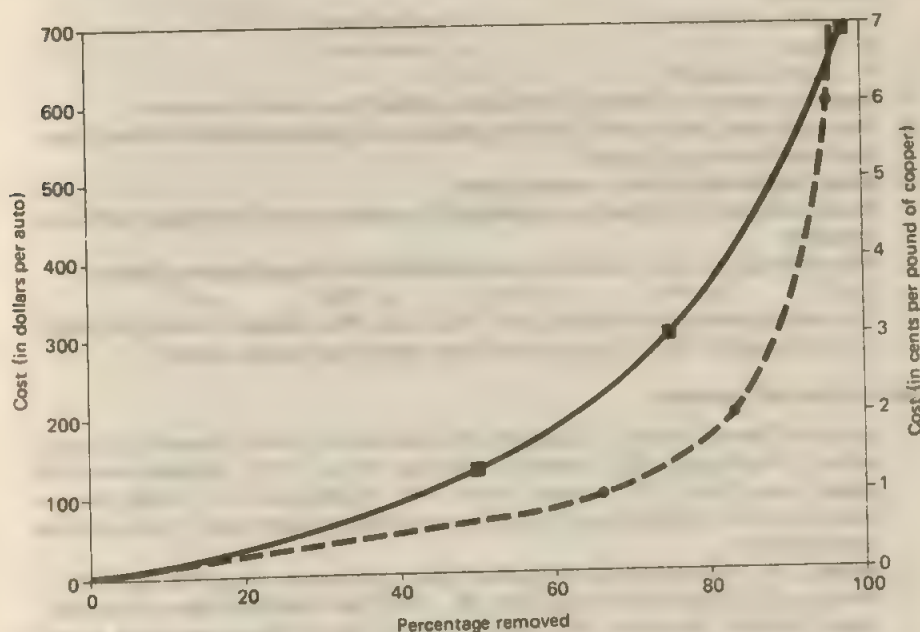


Figure 19.14 Alexander Hamilton's statue suffers soiling from air pollution at the United States Treasury Building in Washington, D.C. The photo was taken 11 April 1966. (Courtesy of the National Air Pollution Administration, Washington, D.C.)

Figure 19.15 The cost of removing pollutants increases exponentially with the percentage of material removed. The broken line shows the cost of removing sulfur dioxide from copper smelter fumes. The solid line shows the cost of reducing automotive emissions.

Problems

1. What are the natural components of air?
2. List the five major primary air pollutants. (Hint: see Table 19.2.) What is the main source of each?
3. What is the effect of each of the following on human health?
 - a. carbon monoxide
 - b. sulfur oxides
 - c. ozone
 - d. particulate matter

4. Air pollution is estimated to cost the United States \$16 billion per year. What is the cost per person? What is the cost per family of four?
5. Natural gas burns much more cleanly than gasoline. Why can't we run our cars on natural gas?
6. What is an atmospheric inversion? How does it contribute to air pollution?
7. How do oxygen atoms, oxygen molecules, and ozone differ in each of the following qualities?
 - a. composition
 - b. structure
 - c. properties
8. What are the two main types of smog? What weather conditions favor each? What are the chemical components of each?
9. Is the electric car a solution to air pollution on a nationwide basis? Within a given city?
10. What is tetraethyllead? Why is it used in gasoline? Why can't it be used in automobiles with catalytic converters?
11. What is synergism? List two air pollutants that act synergistically.
12. How can one lower the level of nitrogen oxide emissions from an automobile (list two ways)? What pollutants are likely to be increased when these adjustments are made?
13. Describe a chemical system for removing sulfur dioxide from stack gases.
14. What is an electrostatic precipitator? How does it work?
15. Why is it difficult to reduce air pollution by putting pollution-control devices on cars? Comment on this problem, taking into consideration the second law of thermodynamics (chapter 12).
16. What are the average and peak concentrations of each of the following in your community?
 - a. carbon monoxide
 - b. ozone
 - c. oxides of nitrogen
 - d. sulfur dioxide
 - e. particulates
17. Does your community have an air-pollution problem? How could it be solved?
18. Do you or your family own a car? If so, what type of pollution-control devices does it have? Are the devices effective?
19. Should students be allowed to smoke in class?
20. Should smoking be allowed in restaurants? In meeting rooms? On buses, trains, and airplanes?
21. Write chemical equations that show how each of the following pollutants is formed.
 - a. CO
 - b. NO
 - c. NO₂
 - d. SO₂
 - e. O₃
22. The average person breathes about 20 m³ of air a day. What weight of particulates would a person breathe in a day if the particulate level were 400 µg per cubic metre?

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chapter 20

Household Chemicals: Helps and Hazards

Would you like to work in a place where poisonous chemicals are used nearly every day? Where toxic vapors and harmful dusts are a common hazard? Where corrosive acids and alkalies are frequently used? Where highly flammable liquids and vapors sometimes ignite and cause painful burns and extensive property damage? You would?? Well, friend, welcome to the typical American home!

Many people regard a chemistry laboratory as a dangerous place stocked with poisons, explosives, and corrosive chemicals. This fear is the often-quoted reason they give for not taking a laboratory course in school. Yet most people are practicing chemists. There are perhaps half a million chemical products available for use in the American home. These range from ammonia (for cleaning) to zeolites (for water softening). The list includes waxes, wax removers, paints, paint removers, toothpaste, rodenticides, detergents, insecticides, spot removers, aspirin, rubbing alcohol, bleaches, baking soda, disinfectants, polishes, abrasives, and many other products.

Many of the chemicals in household products are quite harmless. Others contain highly corrosive acids and alkalies. Some are quite toxic and should be used with extreme caution. Still others are highly flammable and present considerable fire hazards. Some give off toxic vapors or produce harmful dusts. Many cause undesirable changes in the environment when used or discarded.

Extensive use of chemicals in the home has led to an increasing number of accidents. The chemistry laboratory is probably a safer place than many homes. In the laboratory, chemicals usually are used under carefully controlled conditions. By contrast, studies have shown that chemicals often are used in the home without regard to the directions or the precautions given on their labels. Indeed, all too frequently the labels aren't read at all! It is this *misuse* of household chemicals that often ends in tragedy. It would be nice if everyone knew a lot of chemistry. At the very least, *everyone* should read and follow with great care all directions for using household chemicals. Read them before tragedy strikes.

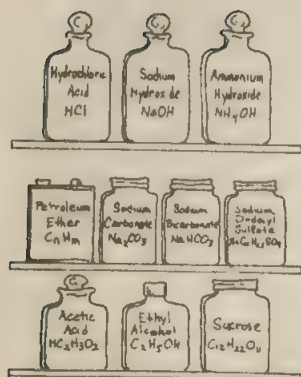


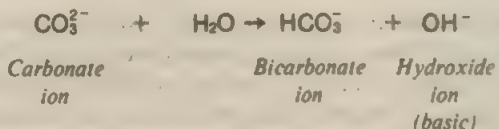
Figure 20.1 A well-stocked chemistry laboratory has a variety of chemicals.

We have already discussed the chemicals that make up our food (chapters 16 and 17). Many of the chemicals used in agriculture (chapter 15) are used in and around the home, too, especially in the yard and garden. We discuss the chemicals we put on our skin and hair (cosmetics) in the next chapter. Chapters 22 and 23 are devoted to the chemicals we use as drugs. There is indeed a great variety of household chemicals. Of all, though, the detergents and related cleaning compounds make up the greatest volume.

A Dirty History of Cleaning

In primitive societies, even today, clothes are cleaned by beating them with rocks in the nearest stream. Sometimes plants, such as the soapworts of Europe or the soapberries of tropical America, are used as cleansing agents. The leaves of the soapwort and soapberries contain saponins, chemical compounds that produce a soapy lather. These saponins were probably the first detergents used.

Ashes of plants contain potassium carbonate (K_2CO_3) and sodium carbonate (Na_2CO_3). The carbonate ion, present in both of these compounds, reacts with water to form an alkaline solution.



The basic solution has detergent properties. These alkaline plant ashes were used as cleansing agents by the Babylonians at least 4000 years ago. Europeans were using plant ashes to wash their clothes as recently as 100 years ago. Sodium carbonate is still sold today as washing soda.

The Romans, with their great public baths, probably did not use any sort of soap. They covered their bodies with oil, worked up a sweat in a steam bath, and then had the oil wiped off by a slave. They finished by taking a dip in a pool of fresh water. And the slaves? They probably didn't bathe at all.

Cleanliness of body and clothes was not very important during the Middle Ages. Neither master nor serf bathed frequently, if at all. Lords and ladies did sometimes mask their body odors with perfumes. And clean outer garments hid the filth of underclothes. Though soap was known, it was used as a medicine, when it was used at all. The discovery of disease-causing microorganisms and subsequent public health practices brought about an increased interest in cleanliness by the late eighteenth century. Soap was in common use by the middle of the nineteenth century.

Grandma's Lye Soap

The first written record of soap is found in the writings of the Roman Pliny the Elder, who described the Phoenicians' synthesis of soap by using goat tallow and ashes. By the second century A.D., sodium carbonate (produced by the evaporation of alkaline water) was heated with lime (from limestone or seashells) to produce sodium hydroxide (lye).



The sodium hydroxide was heated with animal fats or vegetable oils to produce soap (figure 20.3). (Note that soap is a salt of a long-chain organic acid, chapter 11.) The



Figure 20.2 A modern home is stocked with a variety of chemical products. These contain the same chemical substances as those in corresponding positions in figure 20.1.



American pioneers made soap in much the same manner. Lye was added to animal fat in a huge iron kettle. The mixture was cooked over a wood fire for several hours. The soap rose to the surface and, upon cooling, solidified. The glycerol remained as a liquid on the bottom of the pot. Both the glycerol and the soap often contained unreacted alkali, which ate away the skin. Grandma's lye soap is not just a myth!

In modern commercial soapmaking, the fats and oils often are hydrolyzed with superheated steam. The fatty acids then are neutralized to make soap. Toilet soaps usually contain a number of additives such as dyes, perfumes, creams, and oils. Scouring soaps contain abrasives, such as silica, pumice, and oatmeal(!). Many soaps claim to have deodorant action, but few, if any, have any active deodorant (chapter 21) other than the soap itself. The deodorant is just a coverup perfume that quickly fades from the skin. Some soaps have air blown in before they solidify to lower their density so that they float. Some toilet soaps contain—or are made completely of—synthetic detergents. Their action is essentially the same as soap.

Sometimes soaps are made with cations other than sodium ion. Potassium soaps are softer, and they produce a finer lather. They are used alone or in combination with sodium soaps in liquid soaps and shaving creams. Soaps also are made by reacting fatty acids with triethanolamine. These substances are used in shampoos and other cosmetics (chapter 21).

How Soap Works

Dirt and grime usually adhere to skin, clothing, and other surfaces because they are combined with greases and oils—body oils, cooking fats, lubricating greases, and a variety of similar substances—which act a little like sticky glues. Since oils are not miscible with water, washing with water alone does little good.

Soap molecules have a split personality. One end is ionic and dissolves in water. The other end is like a hydrocarbon and dissolves in oils (**figure 20.4**). If we represent the ionic end of the molecule as a circle and the hydrocarbon end as a zigzag line, we can illustrate the cleansing action of soap schematically (**figure 20.5**). The hydrocarbon "tails" stick into the oil. The ionic "heads" remain in the aqueous phase. In this manner, the oil is broken into tiny droplets and dispersed throughout the solution. The droplets don't coalesce because of the repulsion of the charged groups (the carboxyl anions) on their surfaces. The oil and water form an emulsion.

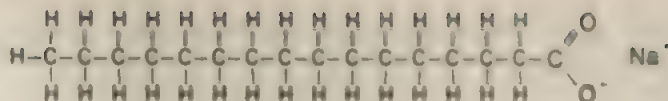


Figure 20.4 Sodium palmitate, a soap (a) Structural formula (b) A schematic representation

(a) *Hydrocarbon end
(dissolves in oils)*

*Ionic end
(dissolves in water)*

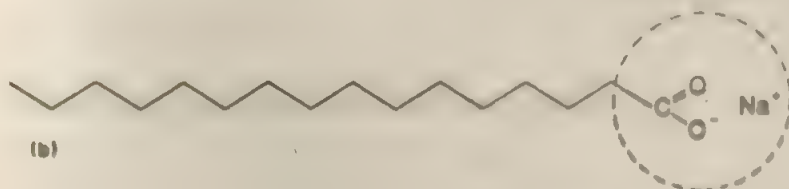
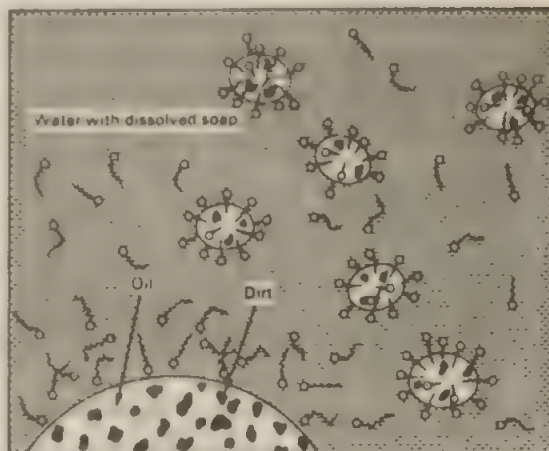


Figure 20.5 The action of soap in removing dirt.



with soap acting as the emulsifying agent. With the oil no longer "gluing" it to the surface, the dirt can be removed easily.

Disadvantages of Soap

For cleaning clothes and for many other purposes, soap has been largely replaced by synthetic detergents because soaps have two rather serious shortcomings. One of these is that, in acidic solutions, soaps are converted to free fatty acids.



A Soap

An acid

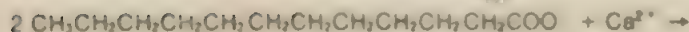


A fatty acid

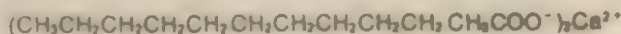
The fatty acids, unlike soap, don't have an ionic end. Lacking the necessary split personality, they can't emulsify the oil and dirt; that is, they do not exhibit any

disadvantage. What is more, these fatty acids are insoluble in water and so separate as a greasy scum.

The second and more serious disadvantage of soap is that it doesn't work very well in hard water. Hard water is just water that contains certain metal ions, particularly magnesium, calcium, and iron ions. The soap anions react with these metal ions to form greasy, insoluble curds.



*Soap
anion*



*Bathub ring
(insoluble)*

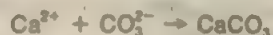
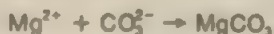
These deposits make up the familiar bathtub ring. They leave freshly washed hair sticky, and are responsible for "bathtub gray" in the family wash.

Water Softeners

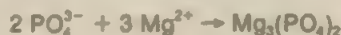
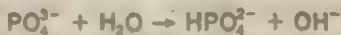
To aid the action of soaps, a variety of water-softening agents and devices have been developed. An effective water softener is washing soda, sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$). It makes the water basic (preventing the precipitation of fatty acids) and removes the hard-water ions, calcium and magnesium. These jobs are performed by the carbonate ion. The ion reacts with water to raise the pH (that is, to make the solution more basic).



The carbonate ion also reacts with the ions that cause hard water and removes them as insoluble salts.



Trisodium phosphate (Na_3PO_4) is another water-softening agent. Like washing soda, it makes the wash water basic and precipitates the calcium and magnesium ions.



In addition, phosphates seem to aid in the cleaning process in some other way, that is not yet well understood.

Water-softening tanks are also available for use in homes and businesses. These tanks contain an insoluble polymeric material that attracts and holds the calcium, magnesium, and iron ions to its surface, thus softening the water. After a period of use, the polymer becomes saturated and must be discarded or regenerated.

Before leaving the subject of soap, let's mention that it has some advantages. It is an excellent cleanser in soft water, it is relatively nontoxic, it is derived from renewable resources (animal fats and vegetable oils), and it is biodegradable. Being

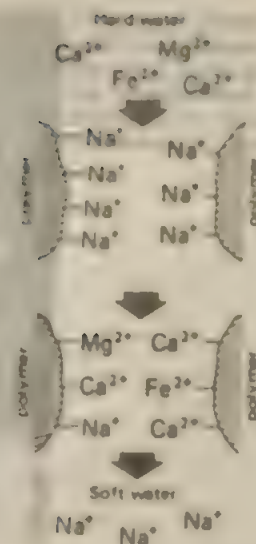
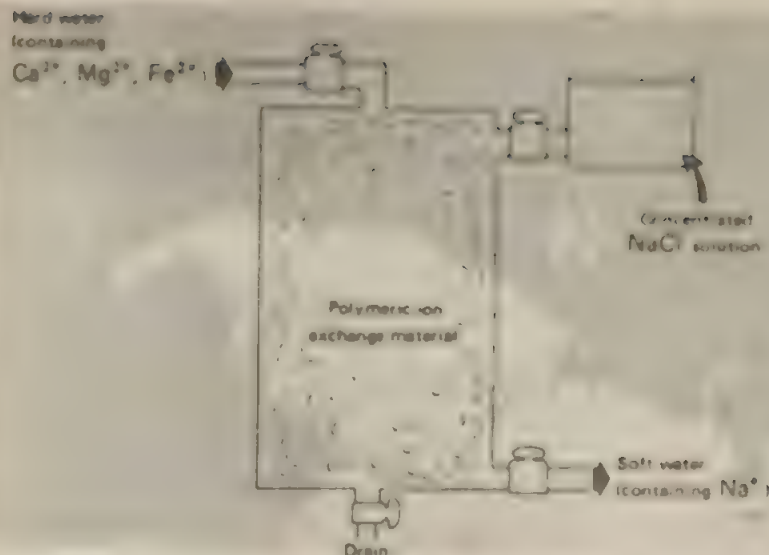
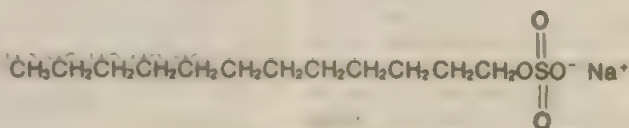
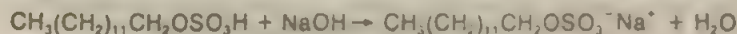
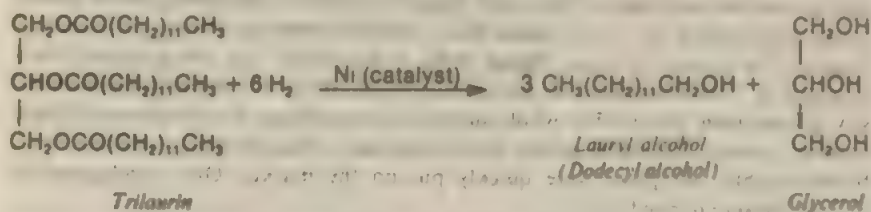


Figure 20-6 One type of water-softening tank contains a polymeric material on which hard-water ions are exchanged for sodium ions. When the material becomes saturated with calcium, magnesium and iron ions, it is regenerated by flushing with a saturated salt solution.

Synthetic Detergents

A second technological approach to the problem of the inadequacy of soap was to develop an entirely new, synthetic type of detergent. The molecules of the synthetic detergents were enough like those of soap to have the same cleaning action but different enough to resist the effects of acids and hard water. Sodium lauryl sulfate is typical of the first (but fairly expensive) synthetic detergents. The first detergents synthesized were derived from fats by reduction with hydrogen, followed by reaction with sulfuric acid, and then neutralization.



Sodium lauryl sulfate
(Sodium dodecyl sulfate)

A black and white photograph showing a large, bright, billowing cloud or plume of smoke or steam. The cloud is irregular in shape, with a thick, rounded base and a more wispy, upward-reaching top. It is set against a dark, grainy, and textured background that appears to be a sky or a large body of water. The lighting is dramatic, highlighting the edges and internal structure of the white mass. The overall image has a vintage, slightly grainy quality.

A black and white photograph showing a hand holding a small, round, light-colored object, possibly a coin or a small cup, against a dark, textured background. The object is held in the lower-left foreground, and its surface appears smooth and reflective. The background is dark and grainy, with some vertical lines and textures visible. The overall image has a high-contrast, somewhat abstract quality.



Figure 20.8 A glass of suds. (Courtesy of Bergwall Productions, New York.)

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{SO}_3^- \text{Na}^+$$

Chapter Twenty

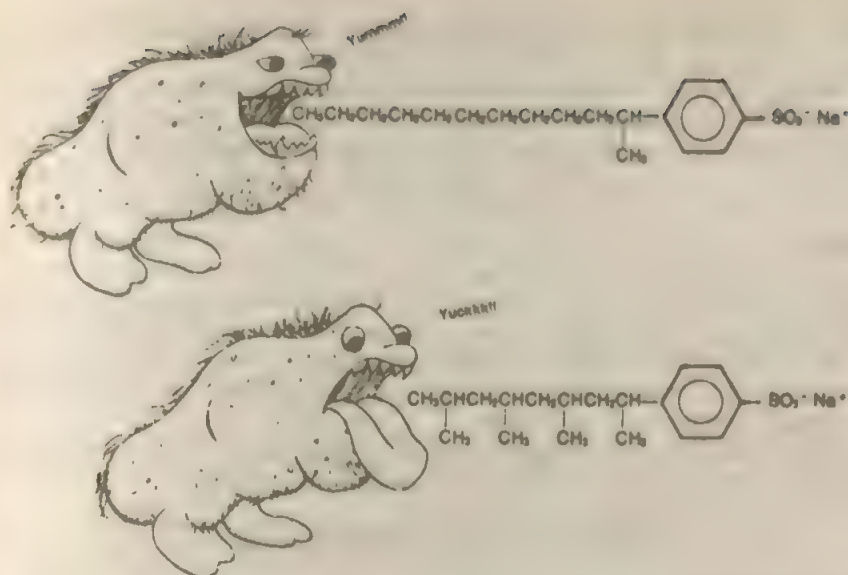


Figure 20.9 Microorganisms can readily digest LAS molecules, but they are unable to break down the branched chains of ABS molecules.

It should be pointed out that just because something is degraded, it doesn't simply disappear. Matter is conserved. Everything's gotta go somewhere. A completely degraded LAS molecule would wind up as carbon dioxide, water, and sulfate (SO_4^{2-}). Barry Commoner (reference 2) contends that degradation of LAS leads to phenol, a toxic material. Commoner maintains that degradable detergents are more likely to kill fish than are nondegradable ones. These allegations are denied by the detergent industry. Who is right? It may be a while before we know.

The cleansing action of synthetic detergents is quite similar to that of soaps. The synthetics work better in acidic solution and in hard water, though. Their calcium and magnesium salts, unlike those of soap, are soluble and therefore do not separate out even in extremely hard water. Thus, the cleansing action of the synthetic detergent is little affected by hard water.

Laundry Detergent Formulations: Phosphates

Even if Barry Commoner is wrong about the toxicity of the degradation products of biodegradable detergents, the laundry detergents that we use do affect streams and lakes. The products for use in homes and commercial laundries usually contain much more than LAS molecules. The LAS is called a surface-active agent, or surfactant. (Any agent, including soap, that stabilizes the suspension of nonpolar substances—such as oil and grease—in water is called a surface-active agent.) In addition to the LAS, modern detergent formulations contain a number of other substances to improve detergency, to bleach, to lessen the redeposition of dirt, to brighten, or simply to reduce the cost of the formulation.

Any substance added to a surfactant to increase its detergency is called a *builder*. Common builders, once widely used but now banned or restricted in many areas, are the phosphates. An example is sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$). It ties up Ca^{2+} and Mg^{2+} in soluble complexes—thus softening the water—and also produces a mild alkalinity, providing a favorable environment for detergent action.

We have seen (in chapter 18) how phosphates speed the eutrophication of lakes. In some areas, phosphates from detergents were shown to be contributing signifi-

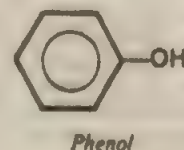


Figure 20.10 Microorganisms, such as the flagellated *Escherichia coli* shown here magnified 42 500 times by scanning electron microscopy, are able to degrade LAS detergents. (Courtesy of Ethyl Corporation, Baton Rouge.)

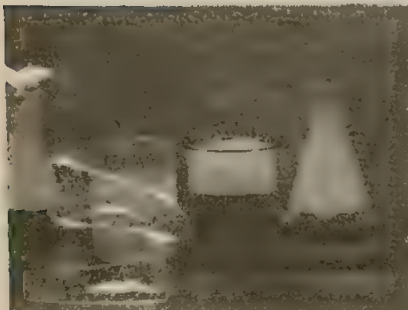
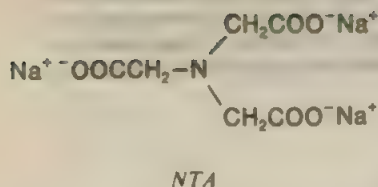


Figure 20.11 Sudsing quality of hard water versus soft water. From the left: (1) detergent in hard water, (2) soap in hard water, (3) soap in soft water, and (4) detergent in soft water. Notice that the sudsing of the detergent differs little in hard and soft water. Notice the absence of sudsing and the formation of insoluble material when soap is used in hard water. (Photo by Lawrence Scott.)

cantly to eutrophication. Although other nutrients, especially nitrates, fertilize the growth of algae, phosphates were often the limiting factor.

Replacements for phosphates were sought. Several reached the market but were soon found to cause problems of their own. Several companies moved to replace part of the phosphates with the sodium salt of nitrilotriacetic acid (NTA). For a few months NTA was hailed as the most likely successor to phosphates. Some questions were raised. NTA was accused of complexing (and thus rendering soluble) such toxic substances as compounds of lead, arsenic, and mercury. The nitrogen in it was shown to end up as nitrate, another nutrient for algae. But the blow that ended the boom was the discovery that a combination of NTA and heavy metals could cause a high incidence of fetal injuries in rats and mice. The federal government recommended a halt in the use of NTA as a detergent builder. Several chemical companies that had hitched their wagon to the NTA star lost millions of dollars of their investments in manufacturing facilities.

Other manufacturers switched to sodium metasilicate (Na_2SiO_3) as a builder. This compound reacts with water to form a strongly basic solution.



Others shifted to sodium perborate ($\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$). This compound, too, forms a strongly basic solution in water.



Hydrogen peroxide (H_2O_2) is liberated and serves as a bleach, decomposing in turn to liberate oxygen.



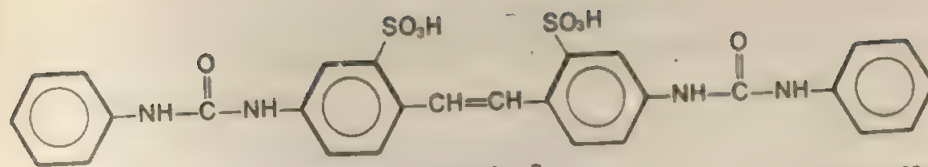
Borates are sometimes toxic. Sodium perborate (2% solution) is used medically as a topical antiseptic. The question of possible damage to the bacteria in sanitary sewage-treatment plants (chapter 18) by widespread use of borates has been raised.

The caustic solutions formed by the phosphate substitutes are quite irritating to the skin. Injuries to children, although few in number, led the Surgeon General to call in 1972 for a return to phosphates. The search for safer builders continues.

Brighter Than Bright

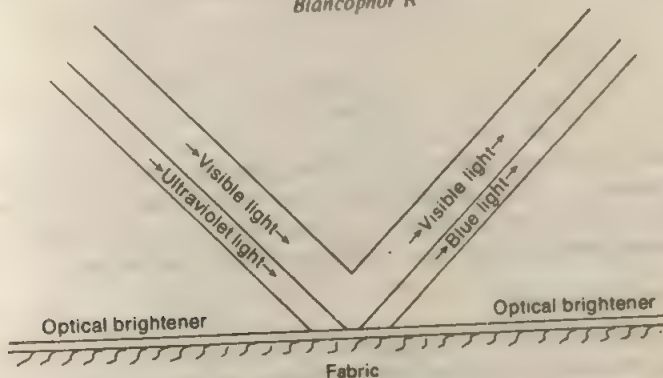
A variety of other additives are used in detergent formulations. Many contain optical brighteners. These compounds, called blanchophors or colorless dyes, absorb the invisible ultraviolet component of sunlight and reemit it as visible light at the blue end of the spectrum. Not only does the fabric appear brighter but the blue light serves to camouflage any yellowing. A diagram of this action, along with the structure of one such dye, is shown in figure 20.12. Clothes treated with an optical brightener on the surface may be dirty underneath, but they look "whiter and brighter than new." These brighteners are also used in cosmetics, paper, soap, plastics, and other products.

Optical brighteners have no known immediate toxic effect on humans. There is some possibility that these compounds might cause cancer or genetic disease. Bjorn Gillberg of the Royal Agricultural College of Sweden has found that brighteners cause minor mutations in microorganisms. Brighteners have been shown to cause skin rashes. Their effect on aquatic systems is largely unknown; yet large amounts are entering our waterways.



Blancophor R

Figure 20.12 An optical brightener, such as the one illustrated, converts invisible ultraviolet light to visible blue light, making the fabric look brighter and masking any yellowing.



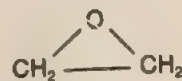
It is important to note that there is little or no known hazard to people from the use of optical brighteners. The only possible benefit of these compounds is a cosmetic one—the appearance of our laundry may be more pleasing. Chemists can make optical brighteners. It is up to the consumer to decide whether the benefit obtained by their use outweighs their monetary, environmental, and health costs.

Liquid Laundry Detergent

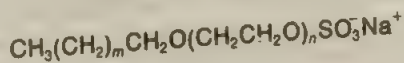
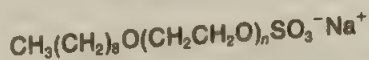
Rapidly rising in the home laundry market are liquid detergent formulations. There are two basic types: those built with phosphates or other additives and the unbuilt ones that are high in surfactant but contain no phosphates or other builders.

LAS is the cheapest and most widely used surfactant in liquid laundry detergents. In unbuilt formulations, LAS usually is used as the sodium or triethanolamine salt. In built varieties, LAS often is present as the potassium salt. The second most popular liquids are the alcohol ether sulfates. These contain a hydrocarbon portion derived from an alcohol (or alkylphenol), a polar portion derived from ethylene oxide, and a sulfate salt portion. These are extremely efficient surfactants, but they are quite expensive.

All the surfactants we have discussed so far, including soap, are *anionic surfactants*; the working part of the molecule is an anion with a nonpolar part and an ionic end. Some liquid detergents contain *nonionic surfactants*. Examples are the alcohol ethoxylates and alkylphenol ethoxylates. The several oxygen atoms, by their attraction for water molecules, make that end of the molecule water soluble, just as the ionic end of an anionic surfactant does.

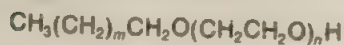
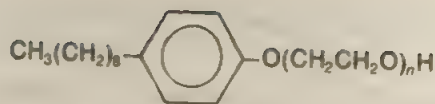


Ethylene oxide



Alcohol ether sulfates

$$\begin{aligned} n &= 7 \text{ to } 13 \\ m &= 6 \text{ to } 13 \end{aligned}$$



Nonionic detergents

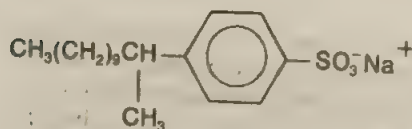
$n = 7 \text{ to } 13$

$m = 6 \text{ to } 13$

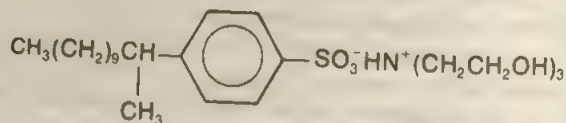
Nonionic surfactants are great for removing oily soil from fabrics. They are not as good as the anionic surfactants at keeping dirt particles in suspension. The alcohol ethoxylates have the unusual property of being more soluble in cold water than in hot. This makes them particularly suitable for cool-water laundering.

Dishwashing Detergents

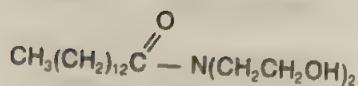
Liquid detergents for washing dishes by hand generally contain one or more surfactants as the only active ingredients. Perfumes, colors, and additives supposed to soften and smooth hands are frequently added. Their main function, though, seems to be the establishment of a base for exaggerated advertising claims. Surfactants used include LAS as the sodium or triethanolamine salt (or both). Some use nonionic surfactants, such as those above. Another nonionic type is the amides made from fatty acids and diethanolamine. Cocamido DEA is an example. Few contain phosphates or other builders. Those that do usually have only small amounts.



LAS, sodium salt



LAS, triethanolamine salt



Cocamido DEA

Most liquid dishwashing detergents differ significantly only in concentration or effectiveness of the surfactant. In any formulation, the surfactant loosens the greasy food residues so that they are easily removed. It also traps the oily mess so that it doesn't redeposit on the dishes. The detergent eventually becomes saturated, though, and breaks down, releasing its greasy load. The weaker the detergent formulation, the sooner it will break down—or the more you will have to use. See reference 3 for a rating of the efficiency of dishwashing liquids.

Detergents for automatic dishwashers are quite another matter. They often are quite caustic and should never be used for hand dishwashing. They contain sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$), sodium metasilicate (Na_2SiO_3), sodium sulfate (Na_2SO_4), a chlorine bleach, and only small amounts of a surfactant, usually a

nonionic type. They depend mainly on their strong alkalies and the vigorous agitation of the machines for the removal of soil.

Bleaches: Whiter Whites

Bleaches were discussed in chapter 8. We won't repeat that discussion here, other than to reemphasize the fact that the major household liquid bleaches are all 4.25% sodium hypochlorite (NaOCl) solutions that differ only in price. For now, let's concentrate on some more complicated compounds that are used in bleaches.

During the early 1950s, hydantoin-type bleaches were introduced. These compounds are stable solids that release chlorine slowly in water. This slow release minimizes damage to fabrics because the concentration of corrosive chlorine is never very high. (Hypochlorite bleaches have all the chlorine available at once and are extremely corrosive in direct contact with fabrics.)

During the late 1950s, cyanurate-type bleaches became available. Like the hydantoin, the cyanurates are dry, stable solids that release chlorine in water. Chlorine release is faster than that of hydantoin bleaches, but slow enough to minimize fabric deterioration.

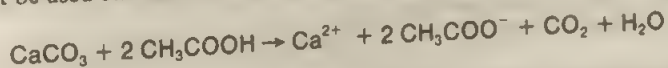
Oxygen-releasing bleaches are usually perborates (p. 294). They are less active than chlorine bleaches and require higher temperatures, higher alkalinity, and higher concentrations to do an equivalent job. They are used mainly for bleaching white, resin-treated polyester-cotton fabrics. These fabrics last much longer with oxygen bleaching than with chlorine bleaching. Also, properly used, the oxygen bleaches get fabrics whiter than do chlorine bleaches.

All-Purpose Cleaning Products

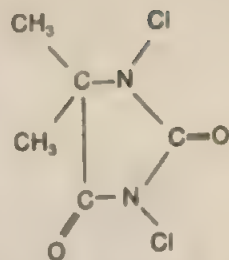
A variety of all-purpose cleaning products are available for use on walls, floors, countertops, appliances, and other tough, durable surfaces. Those for use in water may contain surfactants, sodium carbonate, ammonia, solvent-type grease cutters, disinfectants, deodorants, and other ingredients. Be sure you check the labels on such products. Some are great for certain jobs but not very good for others. They may damage some surfaces while working especially well on others. And most important, they may be harmful to you when they are used improperly.

Household ammonia solutions, straight from the bottle, are good for loosening baked-on grease or burnt-on food. Just soak the object overnight. Diluted with water, household ammonia cleans mirrors, windows, and other glass surfaces. Since both ammonia (NH_3) and water are volatile, no residue remains on the surface. Mixed with detergent, ammonia rapidly removes wax from linoleum. Ammonia vapors are highly irritating. This cleanser should never be used in a closed room. Ammonia should not be used on asphalt tile, wood surfaces, or aluminum. It may stain, pit, or erode these materials.

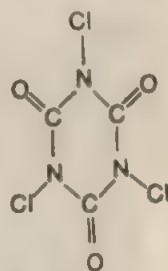
Baking soda (sodium bicarbonate, NaHCO_3), straight from the box, is a mild abrasive cleanser. It absorbs food odors readily, making it good for cleaning the inside of a refrigerator. Vinegar (acetic acid, CH_3COOH) cuts grease film nicely. It should not be used on marble, because it reacts with it, pitting its surface.



Most powdered cleansers contain a hard abrasive such as silica (silicon dioxide, SiO_2) for rubbing dirt loose from a surface. They also usually contain a surfactant to dissolve grease. Some brands also feature a chlorine-releasing bleach. These abrasive cleansers may scratch the porcelain on appliances, plastic countertops, and other surfaces. They may even scratch the surface of sinks, toilet bowls, and bathtubs. Dirt



A hydantoin-type bleach

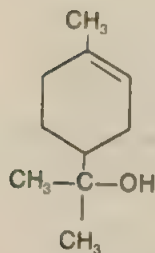


A cyanurate-type bleach

gets in the scratches, making cleaning ever more difficult. Use them with care on surfaces that can withstand the abrasion or on surfaces on which scratches won't matter.

Organic Solvents in the Home

A variety of solvents are used in the home. They may be used to remove paint, varnish, adhesives, waxes, and other materials. Some cleansers also contain organic solvents. Perhaps the best known are those containing pine oil. This oil consists mainly of terpenes, compounds with 10 carbon atoms that occur widely in nature. The pine-oil terpenes usually have a ring structure and one or more alcohol functions. An example is terpineol. Pine oil acts as a mild disinfectant. It also helps to dissolve grease. In moderate concentrations, it has a pleasant odor.



Terpineol

Petroleum distillates are added to some all-purpose cleansers as grease cutters. These are hydrocarbons, much like gasoline, derived from petroleum. They do dissolve grease readily, but, like gasoline, they are highly flammable. They are also deadly when swallowed. The lungs can become saturated with hydrocarbon vapors, fill with fluid, and fail to function.

Most of the organic solvents used around the home are volatile and flammable. Many have toxic fumes; nearly all are narcotic at high concentrations. Many young people, trying to get their kicks from sniffing glue or other solvents, have died of heart failure. Such solvents should be used only with adequate ventilation. They should never be used around a flame. Be sure to read and heed all precautions before using any solvent. And never use gasoline for cleaning; it is too hazardous in too many ways.

Quaternary Ammonium Salts: Dead Germs and Soft Fabrics

Earlier in this chapter, we discussed anionic detergents and nonionic surfactants. There is a third type, called *cationic*, in which the surfactant is a positive ion. The most common of these are called quaternary ammonium salts because they have four groups attached to a nitrogen atom that bears a positive charge. An example of such a cationic surfactant is hexadecyltrimethylammonium chloride.

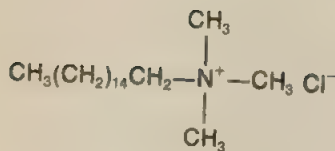
These cationics are not very good detergents, but they have a degree of germicidal action. Sometimes they are used along with nonionic surfactants as cleansers and disinfectants in the food and dairy industries. Cationics cannot be used with anionic surfactants. The ions of opposite charge would come together and cancel one another out.

Another kind of quaternary salt, with *two* long carbon chains and two smaller groups on nitrogen, finds use as a fabric softener. An example is dioctadecyldimethylammonium chloride. These compounds are strongly absorbed by the fabric, forming a film on the fabric's surface one molecule thick. The long hydrocarbon chains lubricate the fibers, imparting increased flexibility and softness to the fabric.

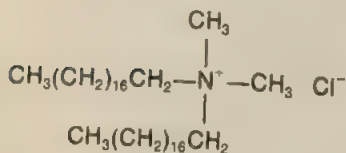
We could extend our discussion of household chemicals almost forever. But all good things must come to an end. You might find it punny that we use fabric softeners as a final touch to this chapter.

Problems

1. Define and give an example (where appropriate, with a structural formula) of each of the following.
 - a. sodium soap
 - b. triethanolamine soap
 - c. ABS detergent
 - d. a builder
 - e. a water softener
 - f. optical brighteners



Hexadecyltrimethylammonium chloride
(A cationic surfactant)



Dioctadecyldimethylammonium chloride

- d. LAS detergent
 - e. nonionic detergent
 - f. cationic detergent
 - j. hypochlorite bleach
 - k. cyanurate bleach
 - l. hydantoin bleach
- 2 How does soap (or detergent) clean a dirty surface?
 - 3 How does an optical brightener work?
 - 4 List the essential ingredients in each of the following household products. (You may wish to consult a chemical formulary [for example, reference 6]. A chemical dictionary [for example, reference 1] may be necessary to identify the chemicals used because formularies often use trade names.) What is the function of each ingredient? What nonessential ingredients are present?
 - a. dishwashing detergent
 - b. all-purpose cleaner (pine-oil type)
 - c. scouring cleaner
 - d. window cleaner
 - e. automatic dishwasher detergent
 - f. oven cleaner
 - g. toilet-bowl cleaner
 - h. liquid drain cleaner
 - i. solid drain cleaner
 - j. paint remover
 5. Give an example of a compound that acts as a fabric softener. How does it work?
 6. What is hard water? How does it affect the action of soap?
 7. The Clearwater Chemical Company announces that it has developed a biodegradable detergent. What tests, if any, should be made before the detergent is marketed?
 8. Maxisuds, Inc., announces that it has found a replacement for phosphate builders in detergents. What tests, if any, should be made before the builder is used in detergent formulations? Should Maxisuds be allowed to market the builder until it is proven harmful? Can a product ever be proven safe?

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chapter 21

Cosmetics: The Chemistry of Charm

Ages ago primitive people used materials from nature for cleansing, beautifying, and otherwise altering their appearance. Evidence indicates that Egyptians, 7000 years ago, used powdered antimony (Sb) and the green copper ore malachite as eye shadow. Egyptian pharaohs used perfumed hair oils as far back as 3500 B.C. Claudius Galen, a Greek physician of the second century A.D., is said to have invented cold cream. Dandy gentlemen of seventeenth-century Europe used cosmetics lavishly, often to cover the fact that they seldom bathed. Ladies of eighteenth-century Europe whitened their faces with lead carbonate (PbCO_3), and many died from lead poisoning.

The use of cosmetics has a long and interesting history, but nothing in the past comes close to the amounts and varieties of cosmetics used by people in the modern industrial world. Each year we spend billions of dollars on everything from hair sprays to toenail polishes, from mouthwashes to foot powders.

What is a cosmetic? The United States Food, Drug, and Cosmetic Act of 1938 defines cosmetics as "articles intended to be rubbed, poured, sprinkled or sprayed on, introduced into, or otherwise applied to the human body or any part thereof, for cleansing, beautifying, promoting attractiveness or altering the appearance. . . ." Soap, although obviously used for cleansing, is specifically excluded from coverage by the law. Also excluded are substances that affect the body's structure or functions. Antiperspirants, products that stop or reduce perspiration, are legally classified as drugs. So are antidandruff shampoos. The main difference between drugs and cosmetics is that drugs must be proved "safe and effective" before they are marketed, while cosmetics generally do not have to be tested before they're marketed.

In this chapter, we take a look at a variety of cosmetics. Emphasis is on those that you or a member of your family are most likely to use.

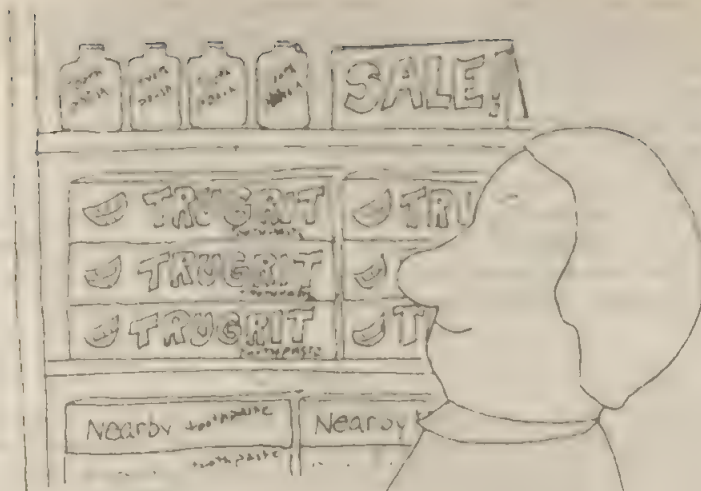


Figure 21.1 Toothpastes are available under many brand names. The only essential ingredients in any toothpaste are a detergent and an abrasive

Toothpaste: Soap with Grit and Flavor

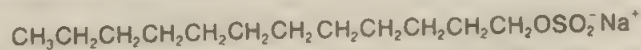
After soap (which doesn't count because the law says it isn't a cosmetic), toothpaste is the most important cosmetic product. The only essential components of toothpaste are a detergent and an abrasive. Soap and sodium bicarbonate would do the job quite well, but they would be rather unpalatable.

The ideal abrasive should be hard enough to clean the teeth but not hard enough to damage the enamel of the teeth. Abrasives frequently used in toothpaste are listed in table 21.1. Some have been criticized as being too harsh.

Table 21.1
Abrasives commonly used in toothpastes

Name	Chemical Formula
Precipitated calcium carbonate	CaCO_3
Insoluble sodium metaphosphate	$(\text{NaPO}_3)_n$
Dicalcium phosphate	CaHPO_4
Titanium dioxide	TiO_2
Tricalcium phosphate	$\text{Ca}_3(\text{PO}_4)_2$
Calcium pyrophosphate	$\text{Ca}_2\text{P}_2\text{O}_7$
Hydrated alumina	$\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$
Hydrated silica	$\text{SiO}_2 \cdot n\text{H}_2\text{O}$

A typical detergent is sodium dodecyl sulfate (sodium lauryl sulfate).



Any pharmaceutical grade of soap or detergent probably would work satisfactorily. Other toothpaste ingredients include sweeteners such as sorbitol, glycerol (glycerin), and saccharin (chapter 17); flavors such as peppermint oil and mint; thickeners such as cellulose gum and polyethylene glycols (PEGs); and preservatives such as sodium benzoate (chapter 17).

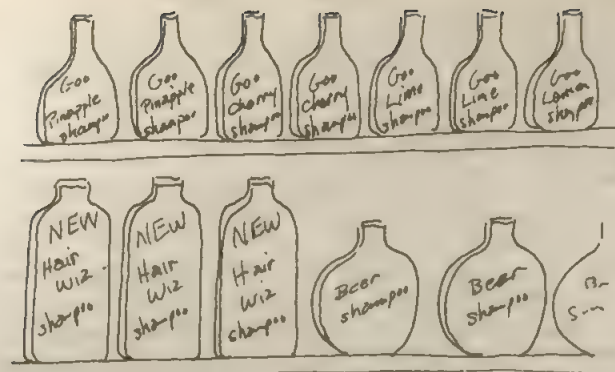


Figure 21.2 Shampoos are available in many forms and colors and under many brand names. The only essential ingredient in any shampoo is a detergent.

Hair is protein, with acidic and basic groups on the protein chain. It stands to reason that the acidity or basicity of a shampoo would affect hair. Hair and skin are slightly acidic. Highly basic (high-pH) or strongly acidic (low-pH) shampoos would damage the hair. More important, such products would irritate the skin and especially the eyes. Most shampoos, however, have pH values between 5 and 8 (reference 11), a difference too slight to affect hair or scalp in any significant way. Shampoos that irritate the eyes usually do so because of other ingredients, not because of too high or too low a pH.

Hair is protein, so protein in shampoos does give the hair more body. Or so the advertisements claim. Some white glues are protein, too. Protein in shampoos literally glues split ends together and coats the hair, making it thicker. If that is what you want, then protein shampoo is for you.

Shampoos for oily or dry hair differ in the relative amounts of detergent in given volumes. Those for oily hair presumably are more concentrated. There seems to be little standardization in formulations from one brand to another (reference 11), however. Shampoos for oily or dry hair seem to be mainly an advertising gimmick.

How about all those flavors and fragrances? Ample evidence indicates that such "natural" ingredients as milk, honey, strawberries, herbs, cucumbers, and lemons add nothing to the usefulness of shampoos or other cosmetics. Why are they there? Smells sell. And there is an appeal to those taken by the back-to-nature movement. There is one hazard to the use of such fragrances: bees, mosquitoes, and other insects like the smell of fruit and flower odors, too. Using such products before going on a picnic or a hike could lead to a bee in your bonnet.

You could make your own shampoo. A possible formulation is given in **table 21.3**. Wet the sodium alginate (a thickener) with the ethyl alcohol, mix thoroughly with the water, and then add the detergent. Do not use alcohol that has been denatured with methyl alcohol or other toxic ingredients.

Table 21.3
A recipe for shampoo

<i>Ingredient</i>	<i>Amount</i>
Triethanolamine dodecyl sulfate	38 mL
Sodium alginate (algin)	2.5 g
Ethyl alcohol	10 mL
Water	62.5 mL

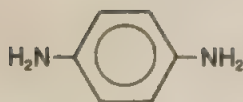
It probably isn't worth it to make your own shampoo. Just buy the cheapest brand of clear liquid shampoo in the store. If you want protein in it, add about 6 cm³ of unflavored gelatin powder per 100 mL of shampoo and mix *thoroughly*. It sets up overnight to a nice gel.

More on Hair: Color and Curl

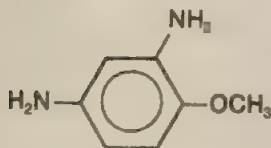
The color of hair and skin is determined by the relative amounts of two pigments. *Melanin* is brownish black. *Phaeomelanin* is the red-brown pigment that colors the hair and skin of redheads. Brunettes have lots of melanin. Blondes have little of either pigment. Brunettes who would like to become blondes can do so by *oxidizing* the colored pigments in their hair to colorless products. Hydrogen peroxide (chapter 8) is the oxidizing agent most frequently employed to bleach hair.

Hair dyeing is a good deal more complicated than bleaching. The color may be a temporary one; water-soluble dyes that can be washed out the next time the hair is washed are sometimes used. More permanent dyes penetrate the hair and remain there. These dyes often are used in the form of a water-soluble, often colorless, precursor that soaks into the hair. The chemical then is oxidized by hydrogen peroxide to a colored compound.

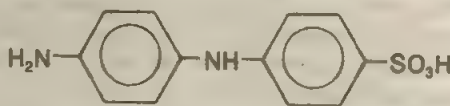
Permanent dyes often are derivatives of an aromatic amine called *para*-phenylenediamine. Variations in color can be obtained by placing a variety of substituents on this molecule. *Para*-phenylenediamine itself produces a black color. The derivative *para*-aminodiphenylaminesulfonic acid is used in blonde formulations. Intermediate colors can be obtained by the use of other derivatives. One such derivative, *para*-methoxy-*meta*-phenylenediamine, and its sulfate salt have been shown to be carcinogenic when fed to rats and mice. The hazard to those who use these dyes to color their hair is not yet known.



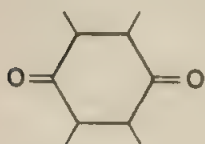
Para-phenylenediamine



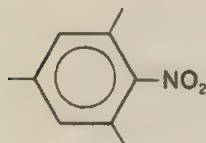
Para-methoxy-*meta*-phenylenediamine



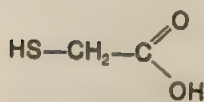
Para-aminodiphenylaminesulfonic acid



A quinone



A nitro compound



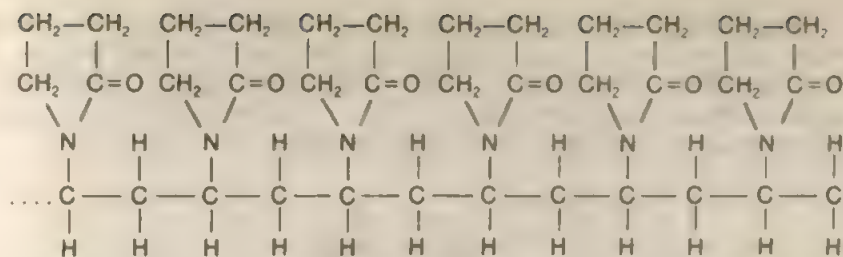
Thioglycolic acid

The chemistry of the colored oxidation products is quite complex. They probably include quinones and nitro compounds, among others. These are well-known products of the oxidation of aromatic amines. It should be noted that even permanent dyes affect only the dead outer portion of the hair shaft. New hair, as it grows from the scalp, has its natural color.

The chemistry of curly hair is also interesting. Hair is protein. Adjacent protein chains are held together by *disulfide linkages* (two sulfur atoms linking the chains). To put a permanent wave in the hair, you use a lotion containing a reducing agent such as thioglycolic acid. This wave lotion ruptures the disulfide linkages (**figure 21.3**), allowing the protein chains to be pulled apart. Then, the hair is set on curlers or rollers and treated with a mild oxidizing agent such as hydrogen peroxide. Disulfide linkages are formed in new positions to give shape to the hair.

The same chemical process can be used to straighten naturally curly hair. The change in hair style depends only on how you arrange the hair after the disulfide bonds have been reduced and before the linkages have been restored. As with permanent dyes, permanent curls grow out as new hair is formed.

Hair can be held in place by using *resins*, solid or semisolid organic materials that form a sticky film on the hair. A common resin used on hair is polyvinylpyrrolidone (PVP).



PVP is dissolved in solvent and sprayed on the hair, where the solvent evaporates. Aerosol sprays, using chlorofluorocarbon propellants (chapter 19), were once widely used. Other, presumably safer, propellants are now employed.

Creams and Lotions: Skin Chemicals

Exposure to sun and wind may leave the skin dry and scaly. Washing too often also removes the natural skin oils. A variety of creams and lotions are available to treat dry skin. An essential ingredient of each is a fatty or oily substance that forms a protective film over the skin. Typical ingredients are mineral oil and petroleum jelly; sometimes both are used in the same preparation. These are mixtures of alkanes obtained from petroleum. Petroleum jelly is a higher-boiling fraction than mineral oil. The former is a semisolid; the latter, a viscous liquid. Other ingredients include natural fats and oils, perfumes, waxes, water, and emulsifiers (compounds that keep the oily portions from separating from the water).

Natural materials used on the skin include lanolin, a fat obtained from sheep's wool, and olive oil. Often, beeswax is added to harden the product.

Some creams have been formulated with hormones, queen bee jelly, and other strange ingredients. None of these has been found to confer any particular benefit. Creams and lotions protect the skin by providing a protective coating and by softening it, much as plasticizers soften plastics (chapter 14). Such skin softeners are called *emollients*. You could just as well use petroleum jelly (one trade name is *Vaseline*) or a good grade of white mineral oil (sometimes called baby oil) as the fancy creams.

It may seem strange that gasoline, a mixture of alkanes, dries out the skin while the higher alkanes in mineral oil and petroleum jelly soften it. Keep in mind, though, that gasoline is a thin, free-flowing liquid. It dissolves the natural skin oils and carries them away. The higher alkanes are viscous. They stay right on the skin and serve as emollients.

Skin moisturizers? The term is undefined. Components called moisturizers are usually petroleum jelly, a mineral oil, or a similar substance. They may serve to keep the skin softer, in part, by physically preventing the loss of moisture through the protective film.

Lipsticks: Castor Oil and Color

Lipstick is quite similar to skin creams in composition. It is made of an oil and a wax. A higher proportion of wax is used than in creams. This is to keep the lipstick firm. Dyes and pigments provide color. The oil is frequently castor oil. Waxes often employed are beeswax, carnauba, and candelilla. Perfumes are added to cover up the unpleasant fatty odor of the oil. Antioxidants are also employed to retard rancidity.

Bromo acid dyes such as tetrabromofluorescein, a bluish red compound, are responsible for the colors of most modern lipsticks. These compounds often are adhered to metal ions to form colored complexes called *lakes*.

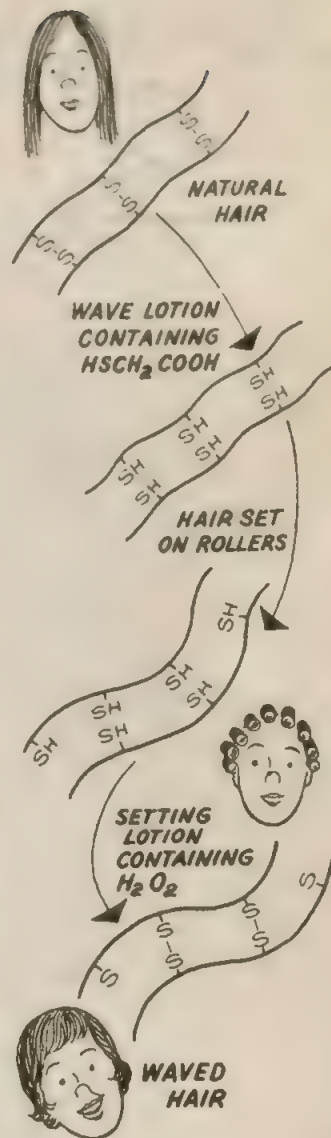
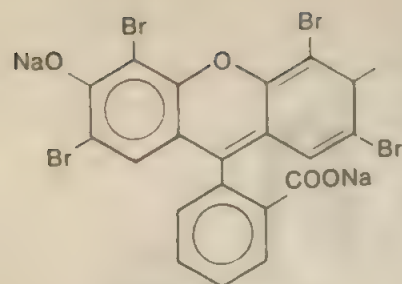


Figure 21.3 The chemistry of the "permanent" waving of hair.



Tetrabromofluorescein

Lipsticks serve to protect the lips as well as to enhance their beauty. You can make your own lipstick. A typical recipe is given in **table 21.4**. Just melt the first three components together on a hotplate. Separately, dissolve the tetrabromofluorescein in the castor oil. Then mix the two solutions and add the perfume. Pour into a suitable mold and allow to harden.

Table 21.4
A recipe for lipstick

<i>Ingredient</i>	<i>Amount</i>
Beeswax, white	3.3 g
1-Hexadecanol (cetyl alcohol)	1.2 g
Sesame oil	2.0 g
Castor oil	2.9 g
Tetrabromofluorescein	0.4 g
Perfume	to suit

Perfumes, Colognes, and Aftershave Preparations

No one wants to smell bad. Many people like to give off the pleasant aroma of a fruit or a flower, perhaps moderated a bit to avoid overwhelming a neighbor's nose. Perfumes are among the most ancient and the most widely used of the cosmetics. Their chemistry, however, is exceedingly complex.

Originally, perfumes were extracted from natural sources. Nowadays, chemists have identified many of the components and synthesized them in the laboratory. The best perfumes, perhaps, are still made from natural materials, for chemists have so far been unable to identify all the many important but minor ingredients.

A good perfume may have a hundred or more constituents. Often, the components are divided into three categories, called *notes*, based on differences in volatility. The most volatile fraction (that which vaporizes most readily) is called the *top note*. This fraction, made up of relatively small molecules, is responsible for the odor when a perfume is first applied. The *middle note* is intermediate in volatility. It is responsible for the lingering aroma after most of the top-note compounds have vaporized. The *end-note* fraction has very low volatility; it is made up of compounds with large molecules.

Several compounds with flowery or fruity odors are synthesized in fairly large quantities for use in perfumes. Some of these, with their approximate odors, are listed in **table 21.5**. Odors vary a great deal with dilution. A concentrated solution (lots of compound in a small amount of water or other solvent) may be unpleasant, while a dilute solution (a small amount in lots of solvent) of the same compound may have a pleasant aroma. Most of the compounds exist in several isomeric forms.

Many of the flowery or fruity odors are sickeningly sweet, even in dilute solutions. Compounds such as the musks often are added to moderate the overall odor. Musks and similar compounds have extremely disagreeable odors when concentrated but often become pleasant at extreme dilution. Several of these are described in **table 21.6**.

The civet cat, from which civetone is obtained, is a skunklike animal of eastern Africa. Its secretion, like that of the skunk, is a defensive weapon. The secretion from musk deer is thought to be a pheromone (chapter 15) used as a sex attractant.

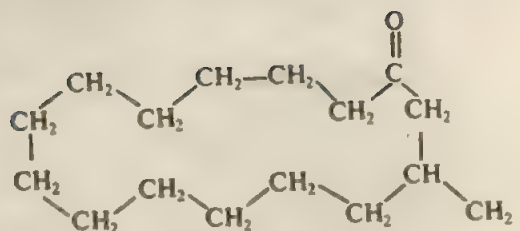
Table 21.5

Name	Structure	Odor
Citral	$\begin{array}{c} \text{CH}_3\text{C}=\text{CHCH}_2\text{CH}_2\text{C}=\text{CHC}=\text{O} \\ \qquad \qquad \qquad \\ \text{CH}_3 \qquad \qquad \text{CH}_3 \end{array}$	Lemon
Ionone	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3-\text{CH} \quad \text{CH} \\ \qquad \quad \\ \text{CH}_2 \quad \text{C} \\ \diagup \quad \diagdown \\ \text{CH} \quad \text{CH}_3 \end{array} \quad \begin{array}{c} \text{CH}=\text{CH}-\text{C}=\text{O} \\ \\ \text{CH}_3 \end{array}$	Violet
Yasmone	$\begin{array}{c} \text{O} \\ \\ \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{C} \\ \qquad \\ \text{CH}_2-\text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3 \end{array} \quad \begin{array}{c} \text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3 \end{array}$	Jasmine
Geraniol	$\begin{array}{c} \text{CH}_3\text{C}=\text{CHCH}_2\text{CH}_2\text{C}=\text{CHCH}_2\text{OH} \\ \qquad \qquad \qquad \\ \text{CH}_3 \qquad \qquad \text{CH}_3 \end{array}$	Rose

Table 21.6

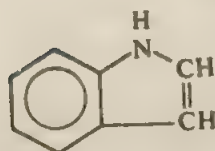
Compound	Structure	Natural Source
Civetone		Civet cat

Muscone

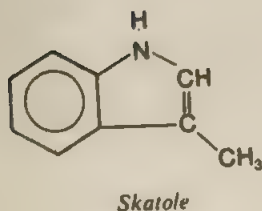


Musk deer

Indole



Feces



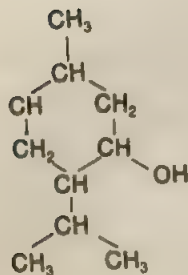
Skatole

Indole and its homolog skatole are principally responsible for the characteristic odor of human feces. These compounds (and others) are now available in synthetic forms.

A perfume usually consists of 10% to 25% odorous compounds and fixatives. The remainder is ethyl alcohol, which serves as a solvent. *Colognes* are diluted perfumes. They often contain only 1% or 2% perfume essence. Thus, colognes are about 10% as strong as perfumes. Dilution can be made with ethyl alcohol alone or with alcohol-water mixtures. **Table 21.7** gives a recipe for a cologne. Just use your favorite perfume. Mix thoroughly. Do not use ethyl alcohol that has been denatured by methyl alcohol or other toxic ingredients.

Table 21.7
A recipe for cologne

<i>Ingredient</i>	<i>Amount</i>
Ethyl alcohol	26 mL
Water	5 mL
Perfume	1 mL



Menthol

Chapter
Twenty-one

It is perhaps of some interest to note that sex attractants have been identified in primates. Indeed, the same set of pheromones (a mixture of organic acids) that operate as sex attractants in rhesus monkeys has been isolated from the vaginal secretions of human females. It is doubtful, however, that such compounds have much influence on human behavior. We probably have overriding cultural constraints. Anyway, we seem to prefer the sex attractant of the musk deer.

Aftershave lotions are quite similar to colognes. Often, menthol is added for a cooling effect on the skin. A typical aftershave lotion recipe is given in **table 21.8**. If undenatured ethyl alcohol is not available, you may substitute rubbing alcohol from the drugstore. Ask the pharmacist what kind to use.

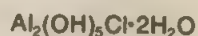
Table 21.8
A recipe for an aftershave lotion

<i>Ingredient</i>	<i>Amount</i>
Ethyl alcohol	75 mL
Water	50 mL
Menthol	0.5 g
Perfume	(to suit)
Food color (your choice)	1 or 2 drops

Perfumes are used to impart a pleasant odor to many products. Some people have allergic reactions to one or more components of perfumes. Before using any cosmetic, you should test your skin for sensitivity to it. Place a drop of the cosmetic on the inside of your elbow. Cover the spot overnight with an adhesive bandage. If there is no reaction (reddened skin or itching) overnight, the product should be reasonably safe for you to use. Stop using *any* cosmetic when any sort of problem develops.

Deodorants and Antiperspirants

Deodorants are formulations of perfumes designed to mask body odor. Antiperspirants stop or retard perspiration. Both serve cosmetic functions, but the antiperspirants work by modifying a body function and so are technically drugs. The active ingredient in nearly all antiperspirants is aluminum chlorohydrate. This compound is an *astringent*; it acts by constricting the openings of sweat glands, thus reducing the amount of perspiration that escapes. The astringent can be dissolved in alcohol for use in an aerosol spray can. It also can be formulated with other ingredients as creams and lotions.



Aluminum chlorohydrate

Sweating is a perfectly natural, healthy function of the body. Stopping it, on a routine basis, is probably not very wise. Body odors arise largely from the hydrolysis of sebum, the natural body oil secreted by sebaceous glands in the skin. The breakdown of sebum forms foul-smelling fatty acids, such as butyric acid. Other compounds, including amines and organic compounds of sulfur, also are formed on the skin. Healthy people who bathe and change clothes daily have little need for deodorants or antiperspirants.

Cosmetics: Economics and Advertising

Most cosmetics are formulated from inexpensive ingredients. Many highly advertised cosmetics are sold at high prices. Are they worth it? That's a value judgment that lies outside the realm of chemistry. If a product makes you look better or feel better what value can be placed on it? Only you can decide.

No attempt has been made here to tell you everything there is to know about cosmetics. Many volumes discussing these interesting chemicals in much more detail are available in libraries. We hope, however, that the knowledge you gained here, coupled with that required on cosmetic labels, will make you a better informed consumer. You need not pay a lot of money for extra ingredients that add a great deal to the cost of a cosmetic but contribute little or nothing to its function.

Problems

1. Read the labels of five brands of toothpaste. List the ingredients of each. If you can, classify each ingredient according to its function; that is, as a detergent, an abrasive, and

so on. You may find a reference book, such as *The Merck Index* (reference 13), to be helpful.

2. Read the labels of five brands of shampoo. List the ingredients in each. Which ingredients are detergents? If you can, tell the function of each nondetergent ingredient.
3. How is hair bleached? What kind of chemical reaction is involved?
4. What is the difference between a temporary and a permanent hair dye? Why is a permanent dye not really permanent?
5. What chemical reactions are involved in curling (or straightening) hair?
6. Read the labels of five brands of lotions or creams (those designed for use on the skin, whether face, hands, or body). List the ingredients of each. If you can, tell the function of each ingredient.
7. Read the labels of five brands of lipstick. List the ingredients of each. If you can, tell the function of each ingredient.
8. What is a perfume? What are the three fractions of a perfume? How do they differ on the molecular level?
9. What is a cologne? How does it differ from a perfume?
10. Read the labels of five brands of aftershave lotion. What are the two major ingredients of each? What other ingredients are present? What is the function of each?
11. What is the difference between a deodorant and an antiperspirant?
12. Read the labels of five brands of antiperspirants. List the ingredients of each. What is the function of each ingredient?

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chapter 22

Body Chemistry: Drugs— From Colds to Cancer

We not only practice chemistry in our homes (chapter 20) and on our skin and hair (chapter 21), we use our bodies as chemical laboratories. There are more than 100 000—and perhaps as many as 500 000—over-the-counter drugs available in the United States. Many others are available with a physician's prescription. We take pills to relieve pain, to cure ailments, and even to calm our anxieties. We take drugs so that we can relax and go to sleep. We take drugs to wake up and stay alert. Some of us take pills to avoid having babies. Some of us take pills to increase our fertility in order to have babies. We even have drugs to counteract the effects of other drugs.

We take drugs that do no good; we take drugs that do great harm. And we pay a lot of money for the privilege, nearly a billion dollars a year for over-the-counter cold remedies alone.

Ours is not the first society to use drugs. The use of chemicals in attempts to relieve pain and cure illnesses dates to prehistoric times. In some societies, the use of drugs was excessive but the variety of drugs was limited. Most societies used ethyl alcohol, a depressant. The use of Indian hemp, or marijuana (*Cannabis sativa*), goes back at least to 3000 B.C. The narcotic effect of the opium poppy was known to the Greeks in the third century B.C. The Indians of the Andes Mountains have long chewed the leaves of the coca plant, *Erythroxylon coca*, for the stimulating effect of the cocaine and the other alkaloids in its leaves. Indians of the southwestern United States have used the flowering heads of the peyote cactus, *Lophophora williamsii*, for their powerful effect as a stimulant. The American Indians also knew how to use Mexican mushrooms (*Psilocybe mexicana* and *Stropharia cubensis*) for their mind-modifying effect. Such use often was connected with religious ceremonies and magical rites.

The use of drugs is not new. What is new is the vast array of drugs available to people in a modern society. Many of these drugs are available without a prescription from the shelves of supermarkets and drugstores. They are "pushed" on television



Figure 22.1 This ancient Greek coin shows an opium poppy capsule. Some cults in ancient Greece worshiped opium. (Courtesy of the Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

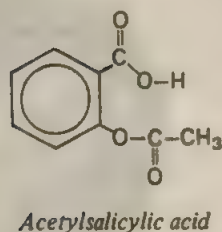
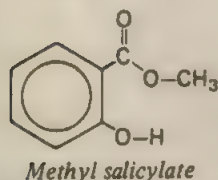
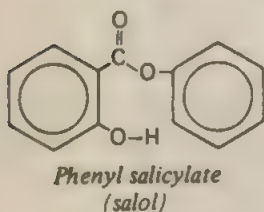
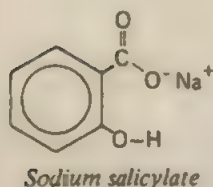
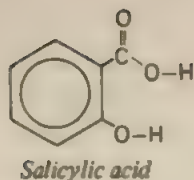


Figure 22.2 Salicylic acid and some of its derivatives.

with the latest Madison Avenue techniques. Illegal drugs in great variety are readily available in most places. Even with prescription drugs, prepared and tested under the supervision of the United States Food and Drug Administration, there are serious problems. Physicians prescribe drugs that had not been discovered when they were in medical school. New drugs are being discovered, tested, and placed on the market each year.

The consumer is faced not only with a nearly infinite variety of products but also with confusing and even contradictory advertising. Is there nothing the buyer can do to sort fact from fiction? It isn't as hopeless as it might seem. There may well be 500 000 over-the-counter drugs, but they are all formulated from only about 250 significant active ingredients. Armed with a few chemical principles, a willingness to read labels, and a reference work such as *The Merck Index* (reference 25), consumers can make intelligent decisions about the drugs they use.

In this chapter, we discuss some of the drugs used to relieve mild pain or discomfort and to treat diseases that affect the body. Drugs that act primarily on the mind—as depressants, stimulants, or “mindbenders”—are left for chapter 23.

The Molecular Architecture of Pain Relievers

Freedom from pain has long been a human goal. Alcohol, opium, cocaine, and Indian hemp (marijuana) were used as medicines for pain relief in some early societies. The first successful synthetic pain relievers were derivatives of salicylic acid (figure 22.2). Salicylic acid was first isolated from willow bark in 1860, although an English clergyman, Edward Stone, had reported to the Royal Society as early as 1763 that an extract of willow bark was useful in reducing fever. Salicylic acid is itself a good *analgesic* (pain reliever) and *antipyretic* (fever reducer), but it is sour and irritating when taken orally. Chemists sought to modify the structure of the molecule to remove this undesirable property while retaining (or even improving) the desirable properties.

The first modification was simple neutralization of the acid (chapter 7). The salt sodium salicylate was first used in 1875. It was less unpleasant to swallow, but it proved to be highly irritating to the lining of the stomach. Phenyl salicylate (salol) was introduced in 1886. It passed unchanged through the stomach. In the small

Table 22.1
Toxicities of some chemicals found in common drugs
(LD₅₀ values are for oral administration of the drug
to rats in milligrams per kilogram of body weight)

Chemical Compound	LD ₅₀
Acetaminophen	3700*
Acetanilide	800
Aspirin	1750
Caffeine	200
Nicotine	55
Phenacetin	1.65
Phenol	530

intestine, it was hydrolyzed to the desired salicylic acid, but phenol (rather toxic, see **table 22.1**) also was formed. Acetylsalicylic acid (aspirin) was first introduced in 1899 and soon became the best-selling drug in the world. Over 40 billion tablets are produced annually in the United States. That's over 200 tablets for each of us.

Another derivative, methyl salicylate (oil of wintergreen), is used extensively as a flavoring agent. It is also used in rubbing compounds. It causes a mild burning sensation when applied to the skin, thus serving as a counterirritant for sore muscles. Methyl salicylate, too, is toxic. As little as 30 cm³ (about 1 oz) has been fatal to an adult.

These derivatives of salicylic acid serve as an excellent example of how variations in structure lead to variations in properties. Some of the new properties are desirable, some are undesirable. We must accept the bad if we wish to take advantage of the good. In the meantime, chemists continue to search for more effective pain relievers, with the goal of minimizing the undesirable side effects while maximizing the beneficial properties.

The Best Aspirin Ever Made

Since aspirin is the most widely used drug in the world, let's take an extensive look at it. Aspirin is a chemical compound. Like other compounds, its properties are invariant. Each aspirin *tablet* usually contains 324 mg (5 grains) of this compound, held together with an inert binder (usually starch). Aspirin has been tested extensively. The conclusions of impartial studies are invariably the same: the only significant difference between brands is their price.

"Buffered" aspirin contains antacids. It is not truly buffered. A *buffer* consumes either acid or base and keeps the pH of a solution essentially constant. The antacids consume acid only; they do not buffer. The experts who evaluated *Bufferin*, the most highly advertised of these products, for the Food and Drug Administration found that there was no basis for the advertising claim that *Bufferin* is "twice as fast as aspirin." Neither did they find evidence that *Bufferin* "helps prevent the stomach upset often caused by aspirin."

Some people experience mild stomach irritation when taking aspirin on an empty stomach. Eating a little food first or drinking a full glass of water with aspirin is just as effective as taking "buffered" aspirin.



Figure 22.3 A wide variety of aspirin, aspirin substitutes, and combination products are available to the consumer.

Arthritis Pain Formula and similar "extra-strength" formulations simply have 7.5 grains of aspirin rather than the usual 5 grains. They have no other active ingredients. Simple arithmetic tells us that three plain aspirin tablets are equal to two *APF* tablets in dosage and are usually much lower in price.

Aspirin relieves minor aches and pains, reduces fever, and suppresses inflammation. It works by reducing the number of pain impulses to the brain. It doesn't cure whatever is causing the pain; it merely kills the messenger. Recent evidence indicates that aspirin acts, at least in part, by inhibiting the synthesis of *prostaglandin* compounds that are involved in inflammation, increased blood pressure, and contractions of smooth muscles. We discuss these fascinating compounds later on a possible "morning-after" birth-control pill.

Aspirin is probably one of the safest and most effective pain relievers known, but it is not without its hazards. Recent studies have indicated that there is some intestinal bleeding every time aspirin is ingested. The blood loss is usually minor (0.5 to 2.0 mL per two-tablet dose) but may be substantial in some cases. Aspirin does inhibit the clotting of blood. It should not be used by people facing surgery, childbirth, or other hazards involving the possible loss of blood for a week before or after the hazards. On the other hand, small doses seem to lower the risk of coronary heart attack and stroke.

Aspirin is not effective for severe pain—for example, pain from a migraine headache. Prolonged use of aspirin, as for arthritic pain, can lead to gastrointestinal disorders. Like all drugs, aspirin is somewhat toxic. It is the drug most often involved in accidental poisonings of children. The toxicities of aspirin and other drugs are listed in **table 22.1**.

Still another hazard associated with the use of aspirin is allergic reaction. In some people, an allergy to aspirin can cause skin rashes, asthmatic attacks, and even loss of consciousness. Some doctors claim that the allergic reaction may be delayed up to 5 hours, so the victim may not associate the reaction with aspirin. Susceptible individuals must be careful to avoid aspirin alone or in any combination with other drugs.

Television Commercials and Other Headaches

The people of the United States spend over \$100 million for aspirin each year. They spend over three times as much on combinations of aspirin and other drugs. Is our money well spent? What are those other drugs? Do they really add anything to the effectiveness of the medication? Must the consumer be at the mercy of false and misleading advertising? These are questions that can be answered rather simply. Let's look first at the chemical compounds in some of the more familiar "combination pain relievers."

For many years, the most familiar combination was aspirin, phenacetin, and caffeine. The APC combination is available under a variety of trade names, such as *Empirin*, *Sal-Fayne*, and *PAC*. It also may be purchased as APC tablets USP, usually at a lower price than the proprietary medications.

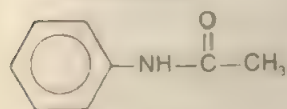
Phenacetin is about as effective as aspirin for reducing fever and relieving minor aches and pains. However, it has been implicated as the source of damage to kidneys and abnormalities of the blood. Perhaps because of its possible side effects, phenacetin has been dropped from the formulas of *Anacin* and *Excedrin*. And, although once an APC formulation, now contains only aspirin and caffeine. Caffeine is a mild stimulant found in coffee, tea, and cola syrup. There does not appear to be any reliable evidence that caffeine enhances the effect of aspirin in any significant way. Indeed, the caffeine may counteract the fever-reducing properties of aspirin. A tablet of *Anacin* does contain a little more aspirin (6.17 grains) than an ordinary 5-grain

tablet. Two *Anacin* tablets give you 12.34 grains of aspirin. You could get the same dose—at a lower price—from just less than two and a half regular aspirin tablets.

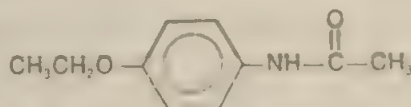
Aspirin Substitutes

Some people who are allergic to aspirin may safely take a substitute compound, acetaminophen. This compound gives relief of pain and reduction in fever comparable to the action of aspirin. However, it may cost 10 times as much as aspirin. It is available by itself under several trade names, such as *Tylenol*, *Dafin*, *Tempra*, and *Nehs*. Some people may be allergic to acetaminophen.

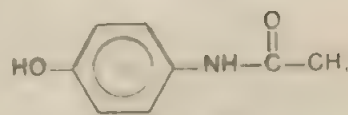
Both phenacetin and acetaminophen are related structurally to acetamide. Acetamide was itself once used widely to reduce fever and to relieve pain. It is highly toxic, however, and has been largely replaced by its safer derivatives and by aspirin.



Acetanilide



Phenacetin



Acetaminophen

How to Cope With (or Vanquish) an Excedrin Headache

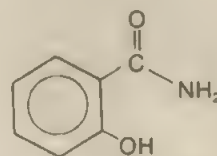
Acetaminophen reduces fever and relieves mild pain. Unlike aspirin, however, it does not reduce inflammation. It is of little help to anyone with arthritis. Acetaminophen also has its side effects. An overdose causes liver damage.

The highly advertised product *Excedrin* contains both aspirin and aspirin substitutes. The latter are acetaminophen and salicylamide. *Excedrin* also contains caffeine. Salicylamide, like aspirin, is a derivative of salicylic acid. Tests have shown it to be only about half as effective as aspirin for the relief of pain. The advertising claim is made that *Excedrin* is more effective than plain aspirin for pain other than headache. It fails to mention that the pain is that suffered by women who have just had babies!

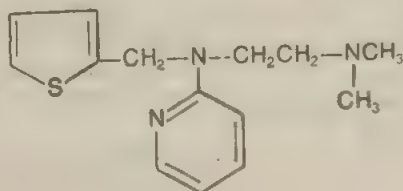
Vanquish, advertised as being "strong medicine," contains aspirin (227 mg), acetaminophen (194 mg), and caffeine (33 mg). The two "gentle buffers" are merely the bases aluminum hydroxide [$\text{Al}(\text{OH})_3$] and magnesium hydroxide [$\text{Mg}(\text{OH})_2$].

Cope is advertised as a "unique formula for relief of nervous tension headaches." It contains aspirin (421 mg), caffeine (32 mg), and magnesium hydroxide, aluminum hydroxide, and an antihistamine! Antihistamines do have the side effect of making you drowsy, but just how they help anyone to "cope" remains a mystery.

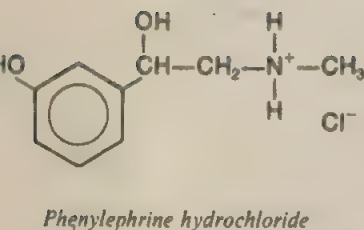
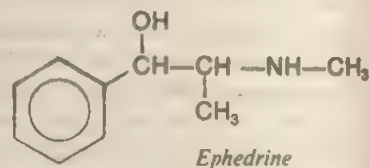
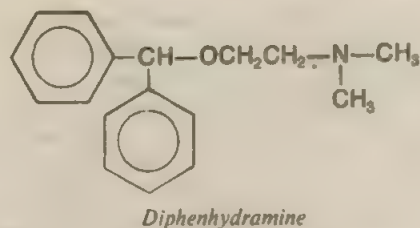
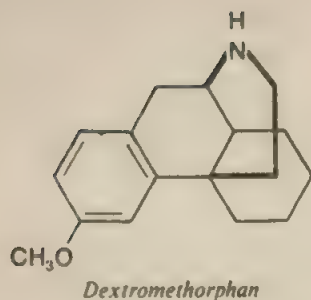
For many years the antihistamine used in *Cope* (and in many over-the-counter sleeping aids, Chapter 23) was methapyrilene. In 1979, the Food and Drug



Salicylamide



Methapyrilene



Chemistry, Chicken Soup, and the Common Cold

We spend a lot of money for cold remedies, but there is no cure for the common cold. Colds are caused by as many as 100 related viruses. No antibiotic or other drug is effective against any of them. If we can't cure colds, why do we use so much medicine for them?

Most cold remedies treat the symptoms. Some, perhaps, give worthwhile relief. None prevent or cure the cold or shorten its duration. Included in the arsenal of weapons used against the cold are cough suppressants, expectorants, bronchodilators, anticholinergics, nasal decongestants, and antihistamines. An advisory panel to the Food and Drug Administration reviewed these compounds in 1976 and came up with some interesting results. Let's take a brief look at each class of medication.

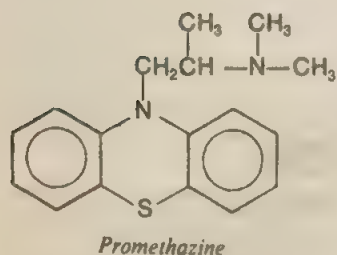
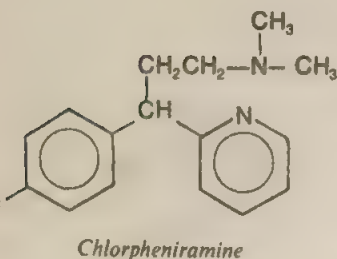
Cough suppressants (antitussives) are available in great variety, but the Food and Drug Administration's panel found only three ingredients safe and effective. Two are narcotics: codeine (chapter 23) and dextromethorphan. The other, diphenhydramine, is an antihistamine. The three effective compounds are available as free bases or as salts. Used as directed, they are safe and effective. However, abuse can lead to addiction.

Expectorants are supposed to help bring up mucus out of the bronchial passages. The panel found none of the products on the market to be safe and effective.

On the other hand, a variety of nasal decongestants were found to be safe and effective when they are used as directed. An example is ephedrine (and its salts). Another nasal decongestant is phenylephrine hydrochloride. Both ephedrine and phenylephrine are bronchodilators.

Several antihistamines were judged safe and effective when they are used as directed. Antihistamines relieve the symptoms of allergies: sneezing, itchy eyes, and runny nose. They were judged *not* to be effective against colds. Examples of safe and effective antihistamines are diphenhydramine hydrochloride, chlorpheniramine, and promethazine hydrochloride.

What should you take for the common cold? Chicken soup is probably as good as anything. Plenty of liquids, plenty of rest, and a week or so of patient suffering are still the best cures. You can gain some relief from the symptoms by using some of the over-the-counter drugs. For an analysis of them by brand name, see reference 3.



Linus Pauling, Vitamin C, and the Common Cold

In chapter 16, we discussed vitamin C (ascorbic acid) as a preventive for scurvy. Only about 40 to 75 mg per day are necessary to prevent this deficiency disease. Daily intake of over 100 mg was thought to be excreted and so wasted.

In 1970, though, Linus Pauling, winner of two Nobel Prizes (for chemistry in 1954 and for peace in 1962), suggested that this vitamin could be used as a weapon against the common cold. He recommended daily doses of 250 to 15 000 mg, depending on the person and the circumstances. Vitamin C, he said, could prevent colds or at least lessen their severity.

Pauling's claims were greeted with skepticism—and even ridicule—by many in the scientific and medical communities. Nevertheless, sales of ascorbic acid zoomed as people rushed to try his plan.

Who was right, Pauling or his critics? The issue still has not been settled. Much research has been undertaken since Pauling's original announcement. Some of it seems to confirm his claims; much of it does not. For example, a recent Canadian study showed that massive doses of vitamin C did not lessen the incidence of colds *per se* but those taking the vitamin missed fewer days of work than those taking a placebo. (A *placebo* is a substance that is made to look and taste like the real thing but that has no active ingredients.) Studies reported in August 1973 showed that no matter how much vitamin C a person swallowed, a maximum of about 200 mg would be retained; the remainder would be excreted. Pauling, however, claims that some people, notably schizophrenics, can absorb incredible amounts of vitamin C without excreting it.

Pauling and his followers are trying to start a new kind of medicine, called *orthomolecular* ("right molecules") medicine. He believes that "having the right molecules in the right amounts in the right place at the right time" is essential to good health. Diets and megavitamin dosages are determined on the basis of extensive chemical tests on an individual's blood and urine.

The effectiveness of such therapy is difficult to measure. Each patient is given a highly individualized regimen to follow. Testing such procedures on large groups in order to get statistically valid data is impossible. It may be years before we know for sure whether Pauling is right or wrong.

Antibiotics: The Age of Miracles

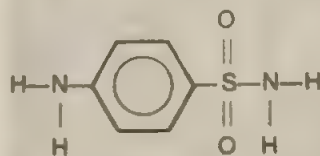
There is no cure for colds, but colds seldom kill. Some bacterial and viral infections are deadly. Half a century ago, infectious diseases were the principal causes of death. By the middle of the 1960s, most of these had been brought under control, largely by the use of a class of drugs called *antibiotics*.* The first successful antibiotics were the sulfa drugs, the prototype of which was discovered in 1935 by the German chemist Gerhard Domagk. Sulfa drugs were used extensively during World War II to prevent infection in wounds. Many soldiers lived who, with similar wounds, would have died in earlier wars.

The mechanism of the action of most drugs is still unknown for the most part. One impressive exception, however, is the action of sulfanilamide, the simplest of the sulfa drugs. Its effectiveness as an antibiotic seems to result from a case of mistaken

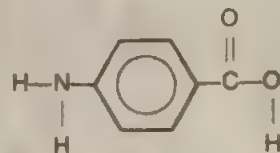
*Strictly speaking, an antibiotic is a soluble substance, derived from a mold or a bacterium, that inhibits the growth of other microorganisms. In everyday usage, however, the term is used to include synthetic chemicals, such as the sulfa drugs, that have the same kind of effect.



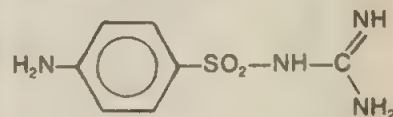
Figure 22.4 Linus Pauling, winner of two Nobel Prizes, advocates massive doses of vitamin C as a preventative for the common cold. (Photo by Margo Moore, San Francisco.)



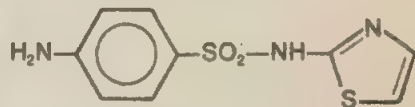
Sulfanilamide



Para-aminobenzoic acid (PABA)



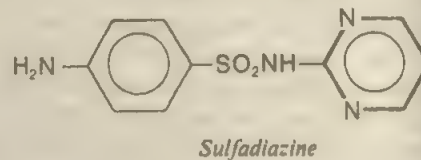
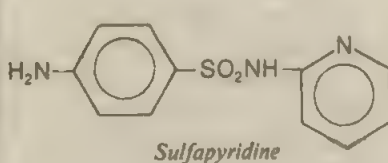
Sulfaguanidine



Sulfathiazole

identity. Bacteria need *para*-aminobenzoic acid (PABA) to make folic acid. Folic acid is essential for the formation of certain compounds the bacteria require for proper growth. But the bacterial enzymes can't tell the difference between sulfanilamide and PABA, because the substances are quite similar in structure. When sulfanilamide is applied to an infection in large amounts, the bacteria incorporate it into a pseudofolic acid. These false molecules cannot perform the growth-enhancing function of folic acid; hence, the bacteria cease to grow.

Sulfanilamide analogs have been developed and tested by the thousands. Only a few are used widely. The structures of several common ones are given here. Introduction of a heterocyclic ring generally increases the activity of a sulfa drug. Some of the sulfa drugs tend to cause damage to the kidneys by crystallizing there. Some present other toxicity problems. For many purposes, sulfa drugs have been replaced by newer antibiotics.



Penicillin: More Miracles

The next miracle drug to appear on the scene was penicillin. This drug was first discovered in 1928, but it was not tried on humans until 1941. Alexander Fleming, a Scottish microbiologist then working at the University of London, first observed the antibacterial action of a mold *Penicillium notatum*. Fleming was studying an infectious bacterium, *Staphylococcus aureus*. One of his cultures became contaminated with blue mold. Contaminated cultures generally are useless. Most investigators probably would have destroyed the culture and started over, but Fleming noted that the bacterial colonies had been destroyed in the vicinity of the mold.

Fleming was able to make crude extracts of the active substance. This material, later called penicillin, was further purified and improved by Howard Florey (an Australian) and Ernst Boris Chain (a refugee from Nazi Germany). Florey and Chain were working at Oxford University. Fleming, Florey, and Chain shared the 1945 Nobel Prize in physiology and medicine for their work on penicillin.

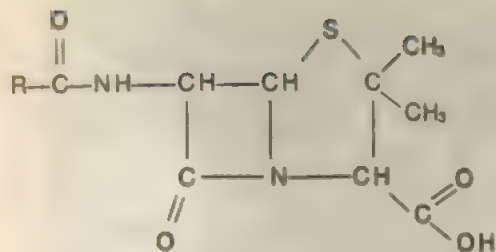
It soon became apparent that penicillin was not a single compound but a group of compounds with related structures. Chemists recognized that, by deliberately designing molecules with different structures, they could vary the properties of the drugs. The penicillins that resulted from these experiments vary in effectiveness. Some must be injected; others can be taken orally. Bacteria resistant to one penicillin may be killed by another. The structures of several common penicillins are shown in figure 22.6.

A knowledge of the structures of drug molecules enables chemists to be much more efficient when they design drugs. However, a knowledge of the structure of the drug molecule is not sufficient for an understanding of the molecular basis of the drug's action. It is also necessary for chemists to understand the structure of the molecules of the human body, of bacteria, and of viruses.

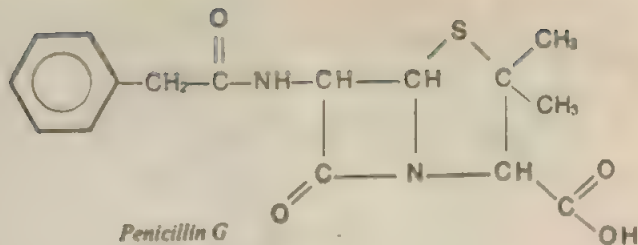
The mode of action of penicillin has only recently been unraveled. In certain bacteria, the cell walls are made up of mucoproteins, polymers in which amino sugars are combined with protein molecules. Penicillin prevents cross-linking between these large molecules and thereby prevents the synthesis of cell walls in



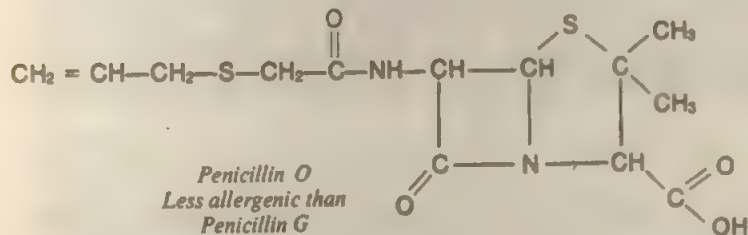
Figure 22.5 Sir Alexander Fleming, discoverer of penicillin. (Courtesy of the Smithsonian Institution, Washington, D.C.)



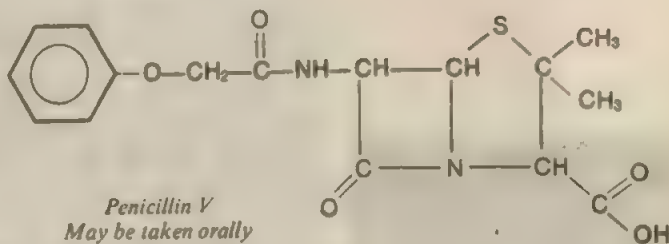
Penicillin
A general formula



Penicillin G
By injection
Side effects: Diarrhea,
allergic reactions may occur



Penicillin O
Less allergenic than
Penicillin G



Penicillin V
May be taken orally
Side effects: similar to
Penicillin G

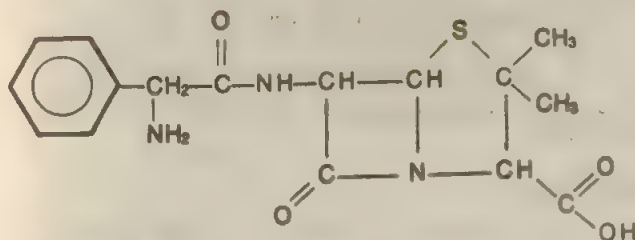
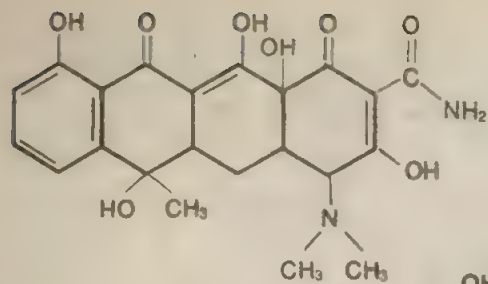


Figure 22.6 Some common penicillins.

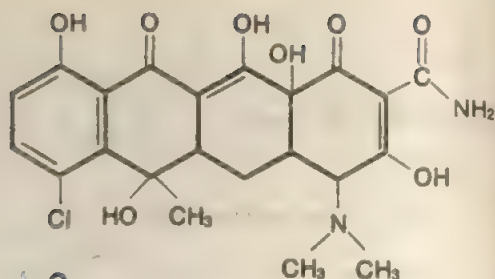
bacteria. Cells of higher animals do not have mucoprotein walls. Instead, they have external membranes that differ in composition from the cell walls of bacteria. These membranes are not affected by penicillin. Thus, penicillin can destroy bacteria without harming human cells. Many people are allergic to penicillin, however, perhaps as many as 5% of the population.

Tetracyclines: Four Rings and Other Things

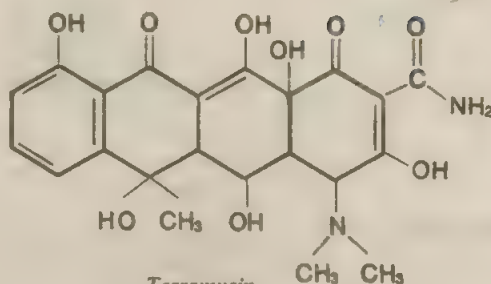
Perhaps the next important development in the field of antibiotics was the discovery of a group of related compounds called *tetracyclines*. The first of these, called *aureomycin*, was isolated in 1948 by Benjamin Duggor from *Streptomyces aureofaciens*. A group of scientists at Pfizer Laboratories isolated terramycin from *Streptomyces rimosus* in 1950 after testing 116 000 different soil samples. Both drugs later were found to be derivatives of tetracycline, a compound now obtained from *Streptomyces viridifaciens*. These three compounds are called *broad-spectrum antibiotics* because they are effective against some viruses as well as bacteria.



Tetracycline



*Aureomycin
(chlorotetracycline)*



*Terramycin
(oxytetracycline)*

There are still a number of viral infections for which we know no cures, including the common cold and infectious hepatitis. Viral genetic material may be involved in some forms of cancer. Some viral infections, such as poliomyelitis, can be prevented by the use of vaccines. Once the disease is contracted, however, there is no cure.

Tetracyclines bind to bacterial ribosomes. This inhibits bacterial protein synthesis and thus blocks bacterial growth. The tetracyclines do not bind to mammalian ribosomes and thus do not affect protein synthesis in host cells. The mode of action of tetracyclines on viruses is not as yet fully known. We can well imagine the progress that will follow after the mechanism of the action of an antiviral drug is known to the extent that the action of sulfanilamide is known. Chemists will be able to design much more effective drugs.

The Age of Miracles: Has It Passed?

During their early history, antibiotics came to be known as miracle drugs. The number of deaths from blood poisoning, pneumonia, and other infectious diseases was reduced substantially by the use of antibiotics. Only four decades ago, a person with a major infection almost always died. Today, such deaths are rare. Four decades ago, pneumonia was a dread killer of people of all ages. Today, it kills only the very old or those quite ill from other causes. The antibiotics have indeed worked miracles in our time. But even the miracle drugs are not without problems. It wasn't long after the drugs were first used that disease organisms began to develop strains resistant to the drugs. Before erythromycin (an antibiotic obtained from *Streptomyces erythreus*) was used very much, all strains of staphylococci could be handled readily by the drug. After it had been put into extensive use, resistant strains began to appear. Staph infections became a serious problem in hospitals. People who had gone to the hospital to be cured got serious bacterial infections instead. Some died from staph infections picked up at hospitals.

A most unwelcomed side effect of the Vietnam war was the spread of a penicillin-resistant strain of gonococcus, the pus-producing bacterium that causes gonorrhea. One of the by-products of war is venereal disease. By the time of the Korean conflict (1950-1953), the problem of gonorrhea had been reduced to little

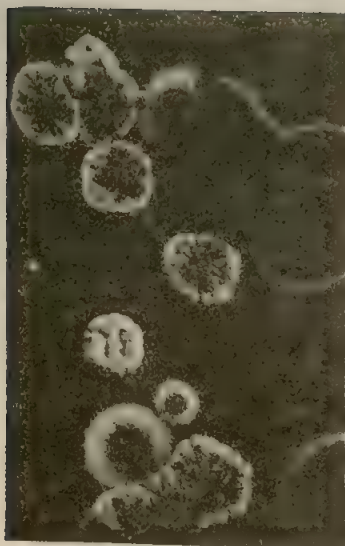


Figure 22.7 Rifampin, an antibiotic used in the treatment of tuberculosis, was developed from this mold colony by a team of Italian scientists from Gruppo Lepetit S.A., a member of the Life Sciences Department of the Dow Chemical Company. (Courtesy of the Dow Chemical Company.)

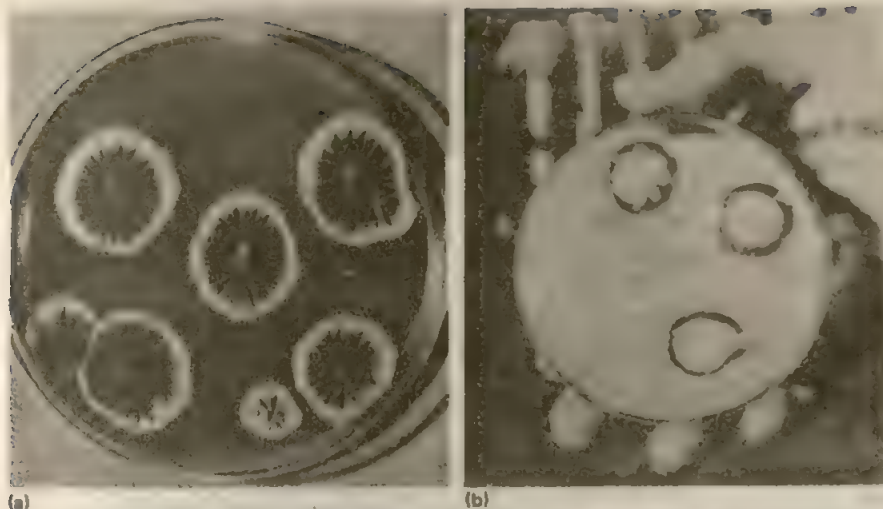


Figure 22.8 (a) Penicillin molds. These symmetrical colonies of green mold are *Penicillium chrysogenum*, a mutant form of which now produces almost all of the world's commercial penicillin. (b) Screening antibiotics for inhibiting effects, scientists placed small discs of blotting paper saturated with an experimental antibiotic solution on the surface of petri dishes seeded with germs. The potency of the antibiotic could be detected by measuring the clear (dark) rings around the discs, which showed that the antibiotic inhibited the germs' growth. (Courtesy of Pfizer Inc.)

more than a nuisance. A few penicillin injections were sufficient to eradicate the infection. The resistant bacteria that developed in Vietnam made gonorrhea a major problem when the soldiers returned home. Health officials referred to the disease as pandemic. Massive and repeated doses of antibiotics were required to control the disease.

There were other ominous signs that all was not well in the age of miracles. Infectious hepatitis became a major problem during the late 1960s. During the early 1970s, hundreds of people in San Antonio, Texas, came down with diphtheria, a childhood disease long considered conquered. Cholera epidemics swept Russia, Italy, and the Near East. Cases of bubonic plague, that scourge of the Middle Ages, were reported in California and New Mexico. Waves of Asian flu swept the world. Flu vaccines were developed but seemed to do little good as new strains of the influenza virus appeared with great frequency.

Are the Dark Ages again descending? Some seem to think so. But a number of the problems posed here have ready explanations and fairly obvious answers. Some of the diseases reappeared because people had grown careless about vaccinations and other simple health precautions. The diseases had been conquered for so long that they were no longer considered threats. And, despite the appearance of new problems and the recurrence of some old ones, we are still way ahead of the game. Science has licked polio. Tuberculosis hospitals are closing. Average life spans are longer than ever. Even the problem of handling drug-resistant strains of bacteria can be solved. It will take a lot of good science to do the job. But, as the structures of chemicals in the human body and in bacteria are worked out in greater detail, it should become possible for us to design more and more specific drugs—another challenging job for chemists in the years ahead.

Hormones: The Regulators

Before we can discuss our next group of drugs, we must take a brief look at the human endocrine system and some of the chemical compounds, called *hormones*, that the system produces. Hormones are chemical messengers produced in the endocrine glands (figure 22.9). Hormones released in one part of the body signal profound physiological changes in other parts of the body. They cause reactions to speed up or to slow down. In this way, they control growth, metabolism, reproduction, and many other functions of body and mind. Some of the more important human hormones and their physiological effects are listed in table 22.2.

Table 22.2
Some human hormones and their physiological effects

<i>Name</i>	<i>Gland and Tissue</i>	<i>Chemical Nature</i>	<i>Effect</i>
Various releasing and inhibitory factors	Hypothalamus	Peptide	Triggers or inhibits release of pituitary hormones
Human growth hormone (HGH)	Pituitary, anterior lobe	Protein	Controls the general body growth; controls bone growth
Thyroid-stimulating hormone (TSH)	Pituitary, anterior lobe	Protein	Stimulates growth of the thyroid gland and production of thyroxin
Adrenal cortex-stimulating hormone (ACTH)	Pituitary, anterior lobe	Protein	Stimulates growth of the adrenal cortex and production of cortical hormones
Follicle-stimulating hormone (FSH)	Pituitary, anterior lobe	Protein	Stimulates growth of follicles in ovaries of females, sperm cells in testes of males
Luteinizing hormone (LH)	Pituitary, anterior lobe	Protein	Controls production and release of estrogens and progesterone from ovaries, testosterone from testes
Prolactin	Pituitary, anterior lobe	Protein	Maintains the production of estrogens and progesterone, stimulates the formation of milk
Vasopressin	Pituitary, posterior lobe	Protein	Stimulates contractions of smooth muscle regulates water uptake by the kidneys
Oxytocin	Pituitary, posterior lobe	Protein	Stimulates contraction of the smooth muscle of the uterus; stimulates secretion of milk
Parathyroid	Parathyroid	Protein	Controls the metabolism of phosphorus and calcium
Thyroxin	Thyroid	Amino acid derivative	Increases rate of cellular metabolism
Insulin	Pancreas, beta cells	Protein	Increases cell usage of glucose; increases glycogen storage
Glucagon	Pancreas, alpha cells	Protein	Stimulates conversion of liver glycogen to glucose
Cortisol	Adrenal gland, cortex	Steroid	Stimulates conversion of proteins to carbohydrates
Aldosterone	Adrenal gland, cortex	Steroid	Regulates salt metabolism; stimulates kidneys to retain Na^+ and excrete K^+
Epinephrine (adrenalin)	Adrenal gland, medulla	Amino acid derivative	Stimulates a variety of mechanisms to prepare the body for emergency action including the conversion of glycogen to glucose
Norepinephrine (noradrenalin)	Adrenal gland, medulla	Amino acid derivative	Stimulates sympathetic nervous system; constricts blood vessels, stimulates other glands
Estradiol	Ovary, follicle	Steroid	Stimulates female sex characteristics; regulates changes during menstrual cycle
Progesterone	Ovary, corpus luteum	Steroid	Regulates menstrual cycle; maintains pregnancy
Testosterone	Testis	Steroid	Stimulates and maintains male sex characteristics

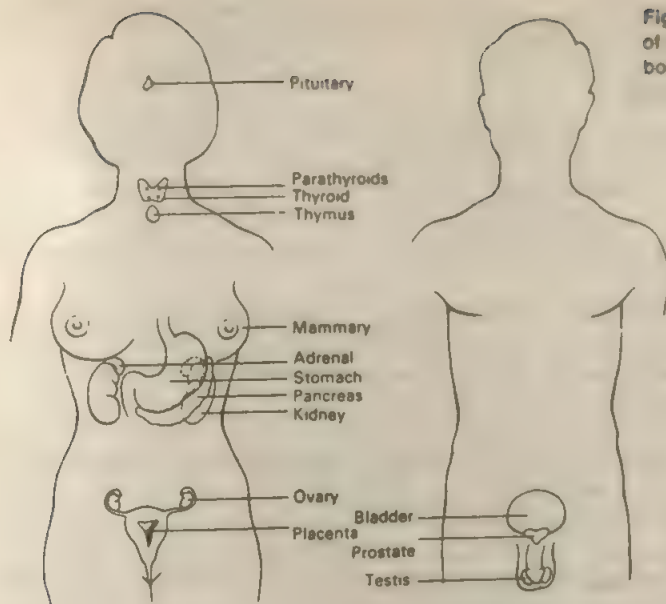


Figure 22.9 The approximate location of the endocrine glands in the human body.

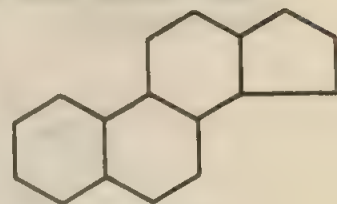
Some of the hormones that affect mental activities are discussed in the next chapter. For now, we concentrate on the steroidal hormones, mainly those involved in the reproductive cycle.

The Steroids: Gallstones, Hardened Arteries, and Good Medicine

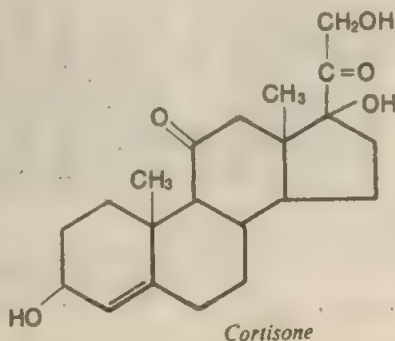
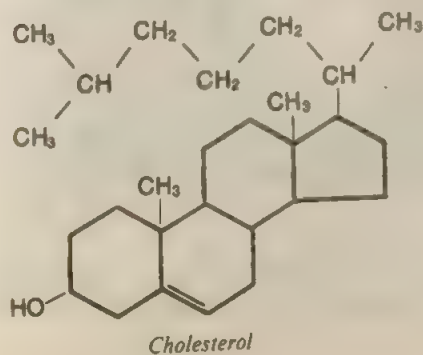
Chemists have spent many years determining the structures of hormones. As indicated in **table 22.2**, some hormones have complicated protein structures. Others are, by comparison, rather simple. The steroids, for example, all have the same carbon skeletal four-ring structure.

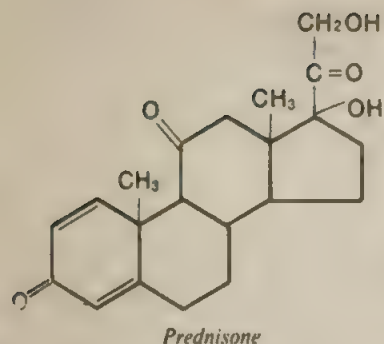
Not all steroids have hormonal activity. Cholesterol is a common component of all animal tissues. The brain is about 10% cholesterol, but its function there is not known. Cholesterol is a major component of certain types of gallstones. It also is found in deposits in hardened arteries; however, studies have not yet established whether cholesterol is there as a cause or as an effect from some other process.

Another steroid of some interest is the adrenal hormone cortisone. Applied topically or injected, cortisone acts in the body to reduce inflammation. It was once widely used in the treatment of arthritis, but relief was transitory and repeated application caused serious side effects. Cortisone has been largely replaced by the



Steroid skeletal structure





related compound prednisone. Prednisone is effective in much smaller doses; thus, its side effects are greatly reduced.

Some Sexy Steroids

Closely related in structure to cholesterol, cortisone, and prednisone are the sex hormones. It is interesting to note that male sex hormones differ only slightly in structure from female sex hormones. In fact, the female hormone, *progesterone*, can be converted by a simple biochemical reaction into the male hormone *testosterone*. The physiological actions of these structurally similar compounds obviously are markedly different.

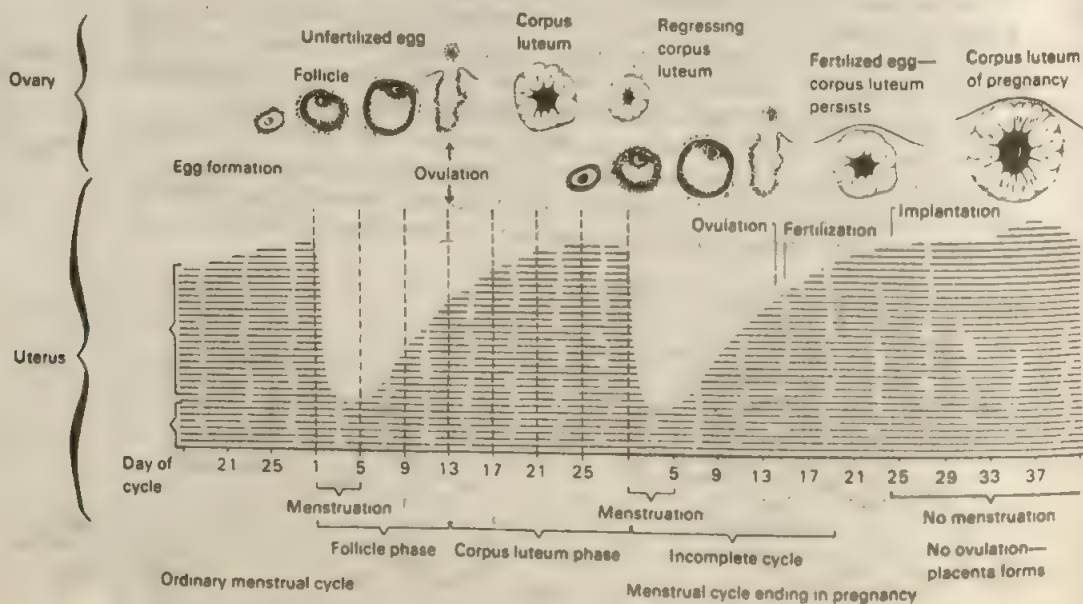
Male sex hormones are called *androgens*. They are secreted by the testes. These hormones are responsible for the development of the sex organs and for secondary sexual characteristics such as voice and hair distribution. The only important male hormone is testosterone.

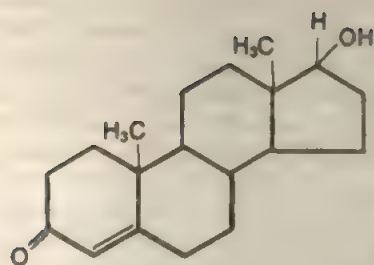
There are two important groups of female sex hormones. The *estrogens* are produced mainly in the ovaries. They control female sexual functions, such as the menstrual cycle and the development of breasts and other secondary sexual characteristics. Two important estrogens are *estradiol* and *estrone*.

The other group of female sex hormones is the *progestins*. The main one of these is progesterone. It prepares the uterus for pregnancy and also prevents the further release of eggs from the ovaries during pregnancy.

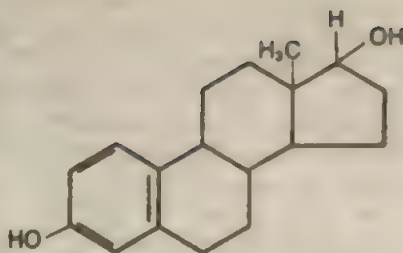
Sex hormones—both natural and synthetic—sometimes are used therapeutically. For example, a woman who has had her ovaries removed may be given female hormones to compensate for those no longer being produced by her ovaries. Some of the earliest compounds employed in cancer chemotherapy were sex hormones. The male hormone testosterone was used to treat carcinoma of the breast in females; estrogens, female sex hormones, were given to males to treat carcinoma of the prostate. Sex hormone therapy is also important for patients who have undergone sex-change operations. After corrective surgery, sex hormones are administered to promote the development of the appropriate secondary sexual characteristics.

Figure 22.10 Changes in the ovary and the uterus during the menstrual cycle. Pregnancy—or the pseudo-pregnancy caused by the birth-control pill—prevents ovulation. (Adapted with permission from Sparks, Philip D.; Nord, Richard P.; Unbehau, Laraine M.; Weeks, Thomas F.; and Hughes, Eileen G., *Student Study Guide for the Biological Sciences*, 3rd ed., Minneapolis: Burgess, 1973.)

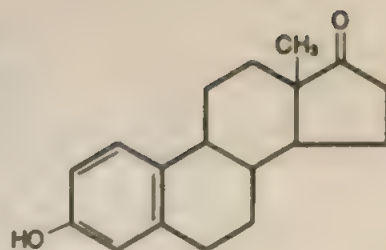




Testosterone



Estradiol



Estrone

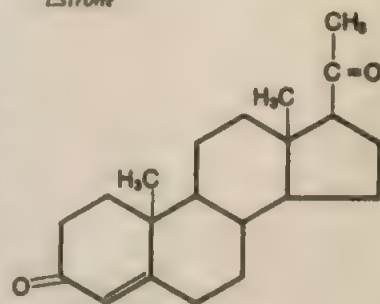
Chemistry and Social Revolution: The Pill

When administered by injection, progesterone serves as an effective birth-control drug. This knowledge led to attempts by chemists to design a contraceptive that would be effective when taken orally.

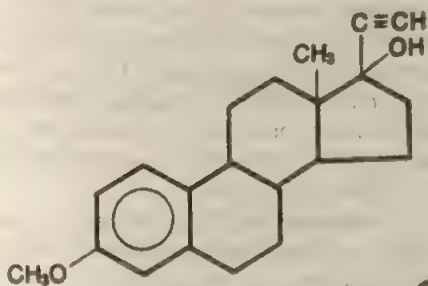
The structure of progesterone was determined in 1934 by Adolf Butenandt. Just 4 years later, Hans Inhoffen synthesized the first oral contraceptive, ethisterone. Ethisterone had to be taken in large doses in order to be effective. It was never widely used as an oral contraceptive.

The next breakthrough came in 1951, when Carl Djerassi synthesized 19-norprogesterone (progesterone with one of its methyl groups missing; note the arrow in the structural diagram). This compound was four to eight times as effective as progesterone as a birth-control agent. Like progesterone itself, it had to be given by injection, an undesirable property. Djerassi then put it all together. Removal of a methyl group made the drug more effective. The ethynyl group ($\text{—C}\equiv\text{CH}$) allowed oral administration. He then synthesized 17 α -ethynyl-19-nortestosterone, mercifully known by the trade name *Norlutin*. This drug proved effective when it was administered orally in small doses.

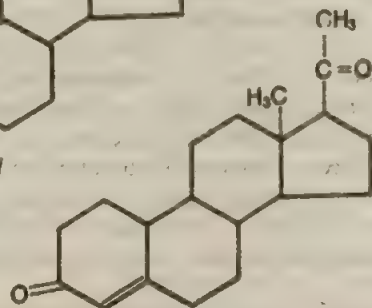
Using the synthetic birth-control steroids then available, an oral medication soon was developed and clinically tested. This medication usually combined an estrogen, such as the synthetic hormone mestranol, with the progestin. The estrogen regulates the menstrual cycle. The progestin acts by establishing a state of false pregnancy. A woman does not ovulate when she is pregnant (or in the state of false pregnancy established by the progestin). Since the woman does not ovulate, she cannot conceive.



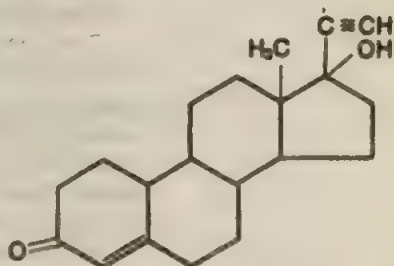
Progesterone



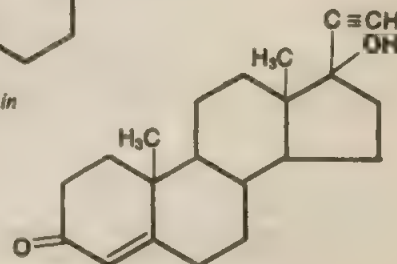
Mestranol



19-Norprogesterone



Norlutin



Ethisterone

The ultimate effects of prolonged tampering with the reproductive biochemistry of the human female remain to be seen. In use in the United States since 1960 by perhaps 15 million women—with about 10 million still using it—the pill appears to be relatively safe. There are undesirable side effects in some women. Among these are hypertension, acne, and abnormal bleeding. The pill also causes blood clotting in some women, but so does pregnancy. Such blood clots can clog a blood vessel and cause death by stroke or coronary heart attack. The deathrate associated with the use of the pill is about 3 in 100 000. This is only 10% of that associated with childbirth—about 30 in 100 000. For the general population, the pill is probably as safe as aspirin. Women who have blood with an abnormal tendency to clot should not take the pill, nor should those who experience any serious side effects. Recently, the Food and Drug Administration has advised women over 40, particularly those who smoke, to use another method of contraception. For these women, the risk associated with using the pill is greater than the risk associated with having a baby. Also, a minipill containing only a small amount of progestin and no estrogen has been marketed. It supposedly avoids many of the problems associated with the combination pill. Most of the undesirable side effects are thought to be caused by the estrogen. In fact, the Food and Drug Administration now requires a warning about the possible harmful effects of estrogens on all drugs containing them.

Unless there are some unforeseen developments in the future, some form of chemical contraceptive seems to be with us to stay. The pill has already brought revolutionary social changes. The impact of science on society is perhaps nowhere more evident.

DES and the Morning After

In 1973, the Food and Drug Administration approved the use of diethylstilbestrol (DES) to induce abortion. The action was surprising to some, because DES had been banned earlier in 1973 as an additive in animal feeds. Cattle fed DES-treated feeds had achieved marketable weights much more rapidly. The DES ban had a major impact on the cattle industry and was not undertaken lightly. The ban came only after a relation between DES and cancer was established. DES had been administered to women with a history of miscarriages in an attempt to prevent spontaneous abortion. No adverse effects were noted in those women. However, 15 years later, an abnormally high incidence of vaginal cancer was noticed among their daughters. This delayed effect emphasizes one of the problems involved in evaluating the possible harmful effects of any chemical.

The Food and Drug Administration had no choice about banning the use of DES in animal feeds. The Delaney clause of the Food and Drug Act of 1958 states clearly that any agent that causes cancer cannot be used in food. Despite efforts to prevent it, DES residues continued to appear in meat from animals that ate feeds containing this additive. More recently, DES has been shown to affect the sons of mothers who took the drug while pregnant. They are more likely to be sterile and to have poorly developed sex organs than the general population.

How could the Food and Drug Administration ban DES from animal feeds and approve its use as an abortifacient? The answer lies in the way the law is written and in the way the chemical is used. The Delaney clause *requires* the banning of any food additive that causes cancer in humans or laboratory animals. DES had been shown to cause vaginal cancer. Therefore, it had to be banned as a food additive. There is no such requirement for drugs; DES could be approved for use in inducing abortions. It also was pointed out that, if the drug were effective, there would be no offspring to have cancer.

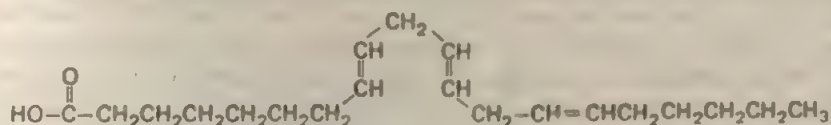
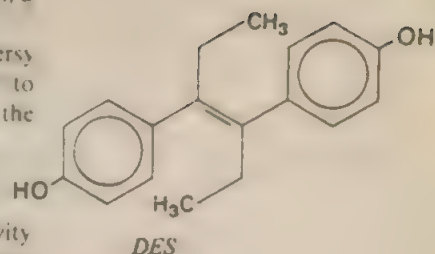
DES is not a steroid. The shape of the molecule shows some similarity to the

structure of estradiol (p 325) Thus, DES is a synthetic female hormone. It was not significantly effective in maintaining pregnancy. And, in order to induce abortion, a women must take large doses. Unpleasant side effects are noted frequently.

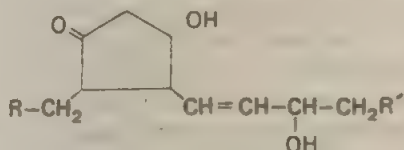
The control of human reproduction is an area subject to great controversy—social, moral, political, and legal. Much more research is needed not only to design new drugs for birth control but to increase our understanding of the biochemistry and physiology of human reproduction.

Prostaglandins: The Latest Miracle Drugs

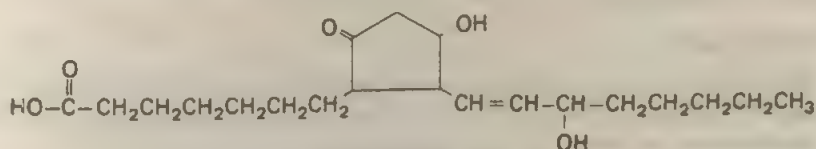
Perhaps no compounds since birth-control pills have stimulated as much activity in pharmaceutical companies as have the group of compounds called *prostaglandins*.



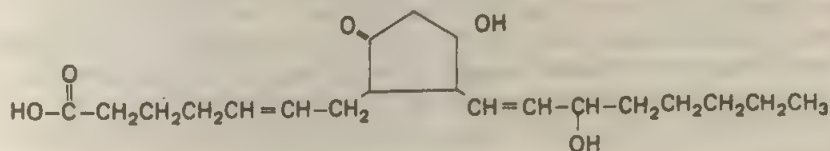
Unsaturated carboxylic acid



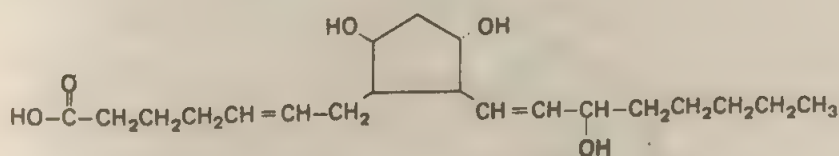
General formula



Prostaglandin E₁



Prostaglandin E₂



Prostaglandin F_{2a}

Figure 22.11 Prostaglandins, the latest of the miracle drugs. The prostaglandins are derived from an unsaturated carboxylic acid having 20 carbon atoms.

Biochemically, prostaglandins are derived from a fatty acid with 20 carbon atoms (figure 22.11). There are six primary prostaglandins; many others have been identified. These compounds are distributed widely throughout the body but at extremely low concentrations. They are among the most potent biological chemicals; they elicit marked changes in the body with extremely small doses.

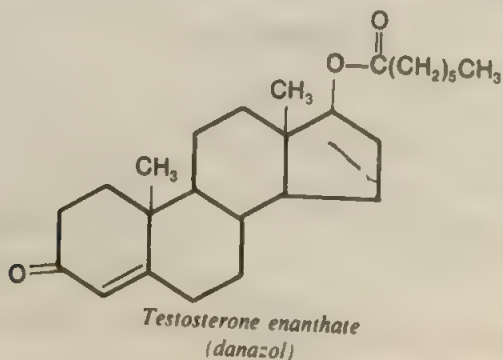
In some respects, the prostaglandins act much as hormones do, regulating such things as smooth-muscle activity, blood flow, and secretion of various substances. This range of physiological activity led to claims that, as drugs, the prostaglandins could relieve nasal congestion, lower blood pressure, alleviate male sterility, relieve peptic ulcers, induce labor, and bring about abortions. The alarming incidence of hypertension in the United States has focused much attention on possible treatments for this condition, and the testing of prostaglandins is one potentially fruitful area of research. It was, however, the prostaglandins' effect as abortifacients that elicited the greatest initial public interest. The compounds had been used to induce abortions in Sweden, Great Britain, and Uganda. The popular press ballyhooed the prostaglandins as a possible morning-after pill. In place of contraceptive measures, it was proposed that a woman who missed her period could immediately take a prostaglandin pill to abort the embryo as a barely visible clump of cells.

What the press did not report was that the drugs had to be administered over a long period of time—8 to 14 hours—by infusion. Far from being a morning-after pill, the drugs had to be injected from a bottle through a needle into a vein, in the same way a patient is given blood. Neither did the press accounts mention the years of research and millions of dollars that researchers would need to take a drug from early testing stages to general availability. Drugs have to be proven relatively safe as well as effective. The intense activity in prostaglandin research certainly indicates that drug companies regard them as having potential not only as abortifacients but also as treatments for emphysema, ulcers, and hypertension. However, it may be years before the potential is realized, if indeed it ever is.

A Pill for Males?

Why do females have to bear the responsibility for contraception? Why not a pill for males? Recent studies have shown that many men—including a majority of the younger ones—are willing to share the risks and the responsibility of contraception.

Actually, a good deal of research has gone into male contraceptives. Estrogens would work, but they would bring about the development of female characteristics in men, including a complete loss of interest in sexual relations with women. One promising drug was abandoned after it was found to turn the eyeballs of men bright red whenever they drank alcohol. The drug company felt that most males would not like to have to choose between avoiding alcohol altogether and having red eyes. Gossypol, a pigment found in cottonseed, has been used in China as a contraceptive for males.



Another problem with developing a pill for men is that we know less about the male reproductive system than we do about the female reproductive system. Carl Djerassi has estimated that research and development of a male contraceptive would take at least 12 years and cost at least \$6 million, perhaps as much as \$30 million. Indeed, a drug called danazol has been tested and found safe and effective. Danazol is testosterone enanthate, administered along with testosterone itself.

Danazol suppresses sperm production. The effect is reversible when the drug is withdrawn. Like the pill for females, danazol often causes weight gain in men. The main problem, however, is that the drug is much too expensive for widespread use. Further, a simple surgical procedure—vasectomy—is available now for males, and the need for a male contraceptive has decreased. A major drawback to vasectomy, however, is that it is usually irreversible. A safe, cheap, effective male contraceptive is still a goal of the drug industry.

Chemicals against Cancer

If chemists can design molecules to relieve headaches, cure infectious diseases, and prevent conception, why can't they do something about cancer? They have done something, but much more remains to be done. Treatment with drugs, radiation, and surgery has led to very high rates of cures for some forms of cancer (e.g., skin cancer). For others, such as lung cancer, the rate is still near zero.

Over 30 different chemical substances are used widely in the treatment of cancer. We can examine only a few representative ones here. First, let's look at a group called antimetabolites.

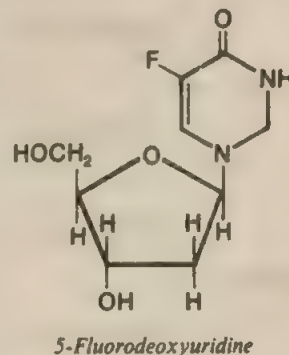
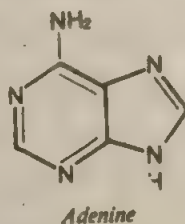
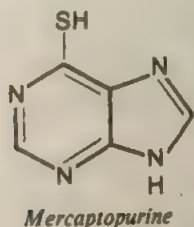
In cancer chemotherapy *antimetabolites* are usually compounds that inhibit the synthesis of nucleic acids. Rapidly dividing cells, characteristic of cancer, require large quantities of DNA. The antimetabolites block DNA synthesis and the increase of the number of cancer cells.

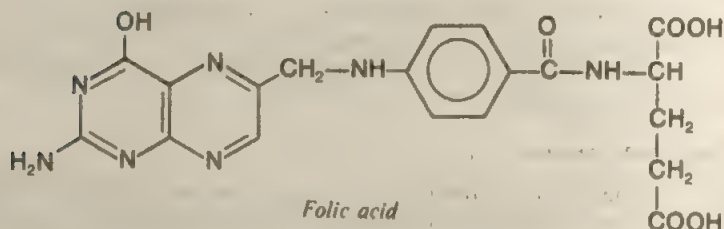
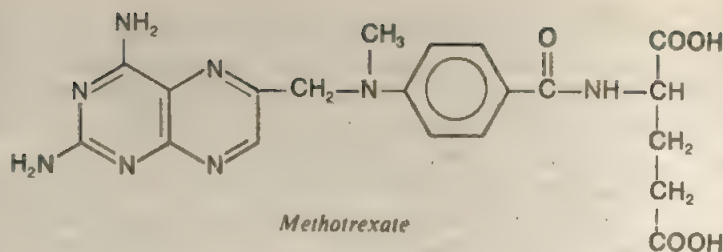
Since cancer cells are undergoing rapid growth and cell division, they generally are affected to a greater extent than are normal cells. Eventually, though, the normal cells are affected to such a degree that treatment must be discontinued.

Two prominent antimetabolites are 5-fluorouracil and its deoxyribose derivative, 5-fluorodeoxyuridine. In the body, both of these can be incorporated into a phosphate-sugar-base unit called a *nucleotide*. The fluorine-containing nucleotide inhibits the formation of a thymine-containing nucleotide required for DNA synthesis. Thus, both compounds slow the division of cancer cells. These compounds have been employed against a variety of cancers, especially those of the breast and the digestive tract.

Another common antimetabolite is 6-mercaptapurine. This compound can substitute for adenine in a nucleotide. The pseudonucleotide then inhibits the synthesis of nucleotides incorporating adenine and guanine. Hence, DNA synthesis and cell division are slowed. 6-Mercaptapurine has been used in the treatment of leukemia.

Another antimetabolite, methotrexate, acts in a somewhat different manner. Note the similarity between its structure and that of folic acid.





Like the pseudofolic acid formed from sulfanilamide, methotrexate competes successfully with folic acid for an enzyme but cannot perform the growth-enhancing function of folic acid. Again, cell division is slowed and cancer growth retarded. Methotrexate is used frequently against leukemia.

Alkylating Agents: Turning War Gases on Cancer

Alkylating agents are highly reactive compounds that can transfer alkyl groups to compounds that are of biological importance. These foreign alkyl groups then block the usual action of the biological molecules. A variety of alkylating agents are used against cancer. Typical among these are the nitrogen mustards, compounds that arose out of chemical warfare research.

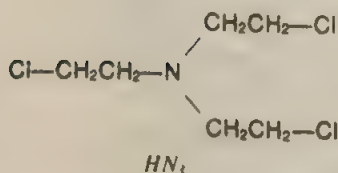
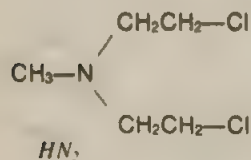
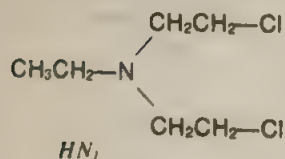
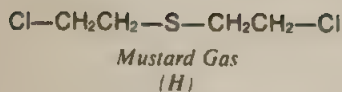
The original mustard "gas" was a sulfur-containing blister agent used in chemical warfare during World War I. The compound is a liquid, but it vaporizes readily. Contact with either the liquid or the vapor causes blisters that are painful and slow to heal. Inhalation of the vapor can cause death. The action of this "gas" is insidious. The effects do not appear for several hours after exposure. It is easily detected, though, by its garlic or horseradish odor. Mustard gas is denoted by the military symbol *H*.

The development of new chemical and biological warfare (CBW) agents continued after World War I. Attempts were made to increase the effectiveness of blister agents by varying their molecular architecture. The nitrogen mustards (symbol *HN*) were developed about 1935.

Though not quite as effective overall as mustard gas, the nitrogen mustards produce greater eye damage and don't have an obvious odor. Structurally, the nitrogen mustards are chlorinated amines.

Fortunately, the use of poison gases has been largely avoided since World War I. The Italians did use mustard gas in their Ethiopian campaign of 1936. The Japanese probably used poison gases against the Chinese in World War II. The Egyptians were accused of using poison gases in Yemen in 1966. The Vietnamese were reported to have used poison gases against the Cambodians in 1978. The major powers, however, have avoided the use of the more lethal chemical and biological agents, despite the fact that they have huge stockpiles of them.

Also, to our happy surprise, the nitrogen mustards have been found to be effective in the treatment of certain types of cancer. We have seen in earlier chapters how on occasion a chemical designed for one (beneficial) purpose was later found to

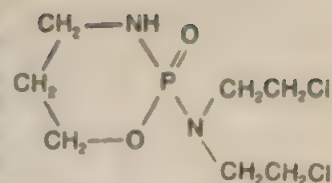


have undesirable side effects. For example, we saw how DDT, once thought to be the perfect insecticide, came under attack for threatening entire species of higher animals. With the nitrogen mustards, we see just the opposite. These molecules, designed for war, have been used most successfully against a formerly fatal type of skin cancer. Dr. Eugene Van Scott of Temple University's School of Medicine announced in 1971 that he had brought about complete remission of some 36 cases of a rare form of skin cancer by bathing the patients in a solution of nitrogen mustards.

This is indeed a striking case of the amoral nature of science. The knowledge that we have of the properties of molecules is neither good nor evil. How we use that knowledge does involve morality. The knowledge can be used either for our benefit or for our destruction. In this respect, science is no different from the social sciences or the humanities.

The nitrogen mustard of choice for cancer therapy nowadays is a compound called cyclophosphamide (*Cytoxan*). It is of interest to note that cyclophosphamide can defleece sheep chemically, saving the high cost of shearing. After treatment with the drug, the wool can be removed almost as easily as taking off an overcoat.

It should be noted that alkylating agents are two-edged swords. They can cause cancer as well as cure it. For example, the nitrogen mustard HN₂ causes lung, mammary, and liver tumors when injected into mice; yet, it can be used with some success in the management of certain human tumors. There is still a lot of mystery—and seeming contradiction—in available data on the causes and cures of cancer.



Cyclophosphamide

Miscellaneous Anticancer Agents

There is a bewildering variety of anticancer agents that defy ready classification. Alkaloids from *Vinca* plants have been shown effective against leukemia and Hodgkin's disease. Actinomycin, a mixture of complex compounds obtained from the molds *Streptomyces antibioticus* and *Streptomyces parvus*, is used against Hodgkin's disease and other types of cancer. It is quite effective but extremely toxic. Actinomycin acts by binding to the double helix of DNA, thus blocking the replication of RNA on the DNA template. Protein synthesis is inhibited.

Sex hormones can be used against cancers of the reproductive system. For example, the female hormones estradiol (a natural hormone) and DES (a synthetic hormone) can be used against cancer of the prostate gland. Conversely, male hormones such as testosterone can be used against breast cancer. Such treatment often brings about a temporary cessation—or even a regression—in the growth of cancer cells. Exactly how the hormones work is still not known.

The food additive butylated hydroxy toluene (BHT) has been shown to be anticarcinogenic in tests involving laboratory animals. Some people involved in cancer research speculate that the use of this additive as a preservative in foods may account for the declining rate of stomach cancer in the United States.

Similarly, there is some evidence that vitamin A may confer a resistance to some cancers. For example, persons suffering from vitamin A deficiencies exhibit a higher incidence of lung cancer. Vitamin C also may have an anticancer function. It has been shown to inhibit the formation of nitrosamines (chapter 17) under conditions similar to those in the human stomach.

Chemotherapy is only a part of the treatment of cancer. Surgical removal of tumors and radiation treatment remain major weapons in the war on cancer. Modern management of cancers can involve surgery, radiation, and one or more anticancer drugs. Indeed, a combination of drugs is often considerably more effective than any one alone. It is unlikely that a single agent will be found to cure all cancers. Steady progress is being made, however. Rates of cure should improve as

research progresses. Perhaps a greater hope lies in the prevention of cancer. Much active research is underway on the mechanisms of carcinogenesis. Once we find the causes, rapid progress toward cures should follow.

Chemotherapy doesn't have all the answers to all human ailments. It probably never will have. Certainly, though, it has helped to give us longer, healthier lives. Let's hear it for chemistry!

Problems

1. Aspirin is a single chemical compound. How may one aspirin *tablet* differ from another?
2. Examine the labels of at least five combination pain relievers. Make a list of the ingredients in each. Look up the properties (medical uses, dosages, side effects, toxicities, etc.) of each in a reference work such as *The Merck Index*.
3. Examine the labels of three over-the-counter sleeping pills (such as *Nitrol*, *Sominex*, and *Sleep-eze*). Make a list of the ingredients in each. Look up the properties (medical uses, dosages, side effects, toxicities, etc.) of the ingredients in a reference work such as *The Merck Index*.
4. Examine the labels of at least three over-the-counter antitension formulations (such as *Cope* and *Compoz*). Make a list of the ingredients in each. Look up the properties (medical uses, dosages, side effects, toxicities, etc.) of the ingredients in a reference work such as *The Merck Index*.
5. Do a cost analysis of five brands of plain aspirin. Calculate the cost per grain (or cost per milligram) of each (1 mg = 0.01543 grains).
6. Compare the cost per grain (or milligram) of an arthritis pain formulation to that of plain aspirin.
7. Examine three liquid cold remedies. What is the alcohol content of each? What other drugs are present? What is the function of each?
8. Examine five cold tablets or cold capsules. What are their active ingredients and what are the functions of the active ingredients?
9. Discuss some of the problems involved in proving a drug safe, and in proving a drug harmful. Which is easier? Why?
10. How can a drug such as penicillin kill bacterial cells without killing human cells?
11. How do sulfa drugs work?
12. What is a hormone?
13. What is an androgen?
14. What is an estrogen?
15. How do birth-control pills work?
16. Tetracyclines are broad-spectrum antibiotics. What does that mean? How do tetracyclines work against bacteria?
17. What is meant by "a resistant strain of bacteria"?
18. List two major classes of anticancer drugs.
19. How does each of these anticancer agents work?
 - a. 5-fluorouracil
 - b. 6-mercaptopurine
 - c. methotrexate
 - d. actinomycin
 - e. alkylating agents

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chapter 23

Chemistry of the Mind: Remedies and Recreation

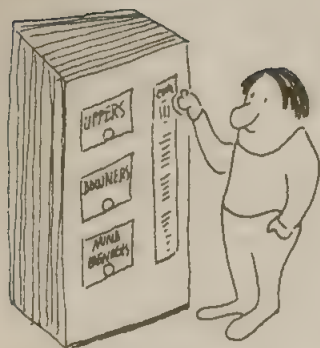


Figure 23.1 We can change our moods by the application of chemicals. Only the milder drugs, such as caffeine and nicotine, are available in vending machines, although many others are easily available from other sources, legal and illegal.

In the preceding chapter, we discussed drugs that affect our bodies—drugs that relieve minor pain and cold symptoms, drugs that cure infectious diseases, drugs that prevent pregnancy, and drugs that cure or slow the growth of cancer. In this chapter, we consider *psychotropic* drugs—those that affect the mind.

There is no clear distinction between drugs that affect the mind and those that affect the body. Probably most of the drugs that we take affect our minds as well as our bodies. Aspirin, sex hormones, even antibiotics may have some influence on our mental state as well as our physical well-being. On the other hand, the narcotic drugs relieve pain at the same time they depress mental activities. In fact, it is becoming increasingly clear that the mind and the body interact closely; they are not separate as people once believed. It can still be useful, however, to distinguish between those drugs that act primarily on the body and those that affect primarily the mind.

Probably the first drugs to be used by primitive peoples influenced the mind. Alcohol, marijuana, opium, cocaine, peyote, and other plant materials have been used for thousands of years. Generally, only one or two of these were used in any one society. Today, however, thousands of drugs that affect the mind are available to us. Some still come from plants, but the great majority are synthetic, brought to you by the creative genius of the chemists of the world.

Drugs can be misused (e.g., using penicillin for a virus infection) and they can be abused (using them for the intoxicating effect). Drug abuse is not just a problem of the young.* We all face difficult decisions about the drugs we use and abuse. Since drugs are chemical substances, perhaps a knowledge of their chemistry would be of help in making those choices.

*There is the story, for example, of the mother who was so upset on hearing that her son had been busted for smoking pot that she had to have a tranquilizer. And the boy's father had to have a double martini to steady his nerves.

Table 23.1
Relationship between drinks consumed, blood alcohol level, and behavior. The data would be approximate for a 70-kg (154-lb) person who is a moderate drinker

<i>Number of Drinks*</i>	<i>Blood-Alcohol Level (percent by volume)</i>	<i>Behavior</i>
2	0.05	Mild sedation; tranquility
4	0.10	Lack of coordination
6	0.15	Obvious intoxication
10	0.30	Unconsciousness
20	0.50	Possible death

*Based on 30-mL (1-oz) "shots" of 90-proof whiskey or 360-mL (12-oz) bottles of beer, consumed rapidly.

Drugs: Up, Down, or Sideways

The drugs that affect the mind can be divided into three classes. The *stimulants* increase alertness, speed up mental processes, and generally elevate the mood. This group, which includes the amphetamines and related compounds, sometimes is referred to as the "uppers." Another category—which includes alcohol, barbiturates, and minor tranquilizers—is the *depressants*. These often are called "downers." They reduce the level of consciousness and the intensity of reactions to environmental stimuli. In general, depressants dull emotional responses. The third category—variously called *hallucinogenics*, *psychotomimetics*, and *psychedelics* because they induce hallucinations, psychoses, and colorful visions—are popularly called the "mindbenders." These drugs don't so much depress or stimulate the mind as they alter qualitatively the way we perceive things. Notable among the mindbenders are LSD, mescaline, and marijuana. Let's examine some of the major drugs in each category.

The Downers: Ethyl Alcohol

There are actually several types of depressants. Some are mild; others can have drastic effects. In every case, the effect depends on many factors, of which the chemical nature of the drug is only one. Such factors as the dosage and the physical and mental characteristics—even the expectations—of the user can profoundly affect the action of a drug.

The most commonly used drug of all is ethyl alcohol. More than two-thirds of the adult population of the United States drink alcoholic beverages at least occasionally. The overwhelming majority do so responsibly. Generally, alcohol may well have been a boon to the human race. It has a long and distinguished record as a mild tranquilizer and sedative. Unfortunately, the nature of people and of alcohol is such that misuse—and abuse—is all too common.

It is estimated that there are about 9 million alcoholics in the United States. These are people so severely addicted that they are unable to hold a steady job or maintain stable family relationships. In addition, over half the fatal automobile accidents involve at least one drinking driver. Babies born to alcoholic mothers often are small, deformed, and mentally retarded. Some investigators believe that this *fetal alcohol syndrome* can occur even if the mothers drink only moderately. Alcohol is by far the most abused drug in the United States.



Figure 23.2 The most widely abused drug of all

Ethyl alcohol is classified as a mild depressant.* It slows down both physical and mental activity. In larger amounts, it can produce unconsciousness or even death. The effects of alcohol are summarized in **table 23.1**. Remember, though, that alcohol's effects vary greatly from one individual to another. They depend on the drinker's weight, the amount of food in the drinker's stomach, the experience of the drinker, and many other factors.

The toxicity of alcohol was discussed in chapter 11. Recently, the mechanism for detoxification was worked out, and the door was opened to an understanding of the mechanism of addiction.

*Although ethyl alcohol generally acts as a depressant, a small amount seems to act sometimes as a stimulant, perhaps by relaxing tensions and relieving inhibitions. Indeed, population studies have shown that those who drink moderately—one or two shots a day—live longer than nondrinkers. Heavier drinking, however, shortens the life span by contributing to diseases of the liver and the cardiovascular system, as well as others.

Snoopy Chemists and the Red Enzyme

Scientists have long been seeking an understanding of the biochemical mechanism of addiction. Unraveling the chemical reactions that occur in the body might bring additional insight into the problem of drug addiction.

An important step forward was made in 1971 with the isolation of a liver enzyme called cytochrome P-450. This enzyme, like hemoglobin, is a red-pigment protein that participates in oxidation reactions in the cell. Cytochrome P-450 is essential to the detoxification of a variety of foreign compounds, including alcohols, some drugs, and pesticides. The red enzyme does not work alone. A second enzyme and a complex fat derivative called a *phospholipid* are also necessary for the successful detoxification of foreign materials. All three compounds have been isolated by a team of researchers headed by Minor Coon at the University of Michigan Medical Center at Ann Arbor.

Large amounts of the red enzyme build up in the liver of a heavy drinker or drug user, enabling it to detoxify large amounts of alcohol (or drugs). This accounts for the tolerance that addicts develop.

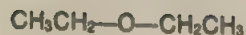
Just as an overdose of insulin requires the diabetic to take some sugar, an overabundance of cytochrome P-450 could require the alcoholic to consume more alcohol. Thus, we are able to propose a chemical mechanism for alcoholism.

The next step is to determine the structure of the red enzyme. Such a study might reveal inherited structural differences in the enzyme molecule, thus explaining why some people become more readily addicted than others to alcohol (and perhaps to other drugs). Once the mechanism of addiction is known, the search for a cure will become more of a science and less of an art.

Anesthetics: Under and Out

Anesthetics are another type of depressant. A *general anesthetic* acts on the brain to produce unconsciousness as well as insensitivity to pain. A *local anesthetic* renders one part of the body insensitive to pain and yet leaves the patient conscious.

Diethyl ether was the first general anesthetic. It was introduced into surgical practice in 1846 by a Boston dentist, William Morton. Inhalation of ether vapor produces unconsciousness by depressing the activity of the central nervous system. Ether is relatively safe. There is a fairly wide gap between the effective level for anesthesia and the lethal dose. The disadvantages are its high flammability and its side effect, nausea.



Diethyl ether



Figure 23.3 An 1802 caricature by James Gillray portraying a lecture demonstrating the effect of ether vapor and nitrous oxide. (Courtesy of the Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

Nitrous oxide, or laughing gas (N_2O), was tried by Morton, without success, before he tried ether. Nitrous oxide was discovered by Joseph Priestley in 1772. Its narcotic effect was noted, and it soon came to be used widely at laughing gas parties among the nobility. Nitrous oxide, mixed with oxygen, finds some use in modern anesthesia. It is quick acting but not very potent. Concentrations of 50% or greater must be used to be effective. When nitrous oxide is mixed with ordinary air instead of oxygen, not enough oxygen gets into the patient's blood and permanent brain damage can result.

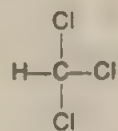
Chloroform was introduced as a general anesthetic in 1847. Its use quickly became popular after Queen Victoria gave birth to her eighth child while anesthetized by chloroform in 1853. Chloroform was used widely for years. It is nonflammable and produces effective anesthesia, but it has a number of serious drawbacks. For one, it has a narrow safety margin; the effective dose is close to the lethal dose. It also causes liver damage. It must be protected from oxygen during storage to prevent the formation of deadly phosgene gas (chapter 7).

Divinyl ether was suggested as an anesthetic in 1930. It is about seven times as effective as ethyl ether. It also acts more rapidly but has the disadvantage of reaching too deep an anesthesia too rapidly. Like its relative diethyl ether, divinyl ether is extremely flammable.

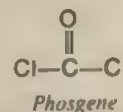
The most potent anesthetic gas, cyclopropane, was first used at the University of Wisconsin General Hospital, Madison, in 1934. Small amounts rapidly produce insensitivity to pain without rendering the patient unconscious. The great drawback is that cyclopropane forms explosive mixtures with air throughout its effective range of concentrations. Special equipment and an experienced anesthetist are required for its use.

Modern anesthetics include fluorine-containing compounds such as halothane, enflurane, and methoxyflurane. These compounds are nonflammable and relatively safe for the patient. Their safety, particularly that of halothane, for operating room personnel, however, has been questioned. For example, female workers suffer a higher rate of miscarriages than does the general population.

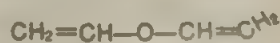
Modern surgical practice has moved away from the use of a single anesthetic.



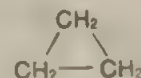
Chloroform



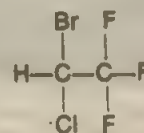
Phosgene



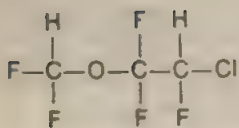
Divinyl ether



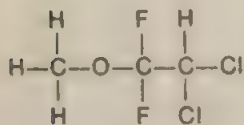
Cyclopropane



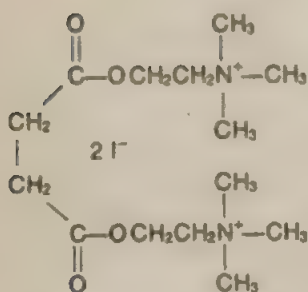
Halothane



Enflurane



Methoxyflurane



Succinylcholine iodide

(Compare acetylcholine, p. 367)

Generally, a patient is given a strong sedative such as thiopental (p. 341) by injection to produce unconsciousness. The gaseous anesthetic then is administered to provide insensitivity to pain and to keep the patient unconscious. A relaxant, such as curare* or succinylcholine iodide, also may be employed. These compounds produce complete relaxation; thus, only light anesthesia is required. This practice avoids the hazards of deep anesthesia.

Nearly all gaseous and volatile-liquid organic compounds exhibit anesthetic action. (Methane [chapter 10] is an exception; it appears to be physiologically inert. Nitrous oxide is the only common inorganic anesthetic.) It is the anesthetic action of organic solvents that leads to their abuse. Sniffing glue solvents, gasoline, aerosol propellants, and other inhalants is perhaps the deadliest form of drug abuse. The dose required for intoxicification is not far from that which would stop the heart. And it is difficult to measure a dose from a plastic or paper bag—the usual method of “glue sniffing.” Also, as with nitrous oxide, sublethal doses can cause permanent brain damage by cutting down the oxygen supply to the brain.

Support Your Local Anesthetic

For dental work and minor surgery, it is usually desirable to deaden the pain in one part of the body only. The first local anesthetic to be used successfully was cocaine. This drug was first isolated in 1860 from the leaves of the coca plant (figure 23.4). Its structure was determined by Richard Willstätter in 1898. Even before Willstätter's work, there were attempts to develop synthetic compounds with similar properties. Cocaine is a powerful stimulant. Its abuse is discussed later in this chapter.

Certain esters of *p*-aminobenzoic acid act as local anesthetics. The ethyl and *n*-butyl esters are used to relieve the pain of burns and open wounds. These are applied as ointments, usually in the form of picrate salts.

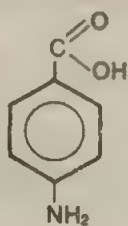
More powerful in their anesthetic action are a series of derivatives with a second nitrogen atom in the alkyl group of the ester. Perhaps the best known of these is procaine (*Novocaine*), first synthesized by Alfred Einhorn in 1905. Procaine can be injected as a local anesthetic. It also can be injected into the spinal column to deaden the entire lower portion of the body. Procaine works by blocking nerve impulses to the brain. When the block involves the spinal cord, messages of pain from the lower parts of the body are prevented from reaching the brain.

*Curare is the arrow poison used by South American Indian tribes. Actually, there are three curares, tube, pot, and gourd curare, named from the type of container in which they are stored. The three curares are obtained from different plants. The one used in conjunction with anesthesia is obtained from *Chondrodendron tomentosum*.

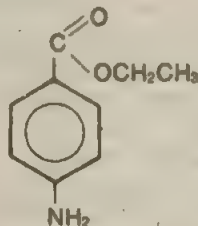
Large doses of curare kill by causing a complete relaxation of all muscles. Death occurs because of respiratory failure.



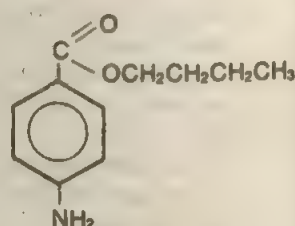
Figure 23.4 Coca leaves and illicit forms of cocaine. (Courtesy of the Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)



p-Aminobenzoic acid



Ethyl *p*-aminobenzoate
(Benzocaine)



n-Butyl *p*-aminobenzoate
(Butesin)

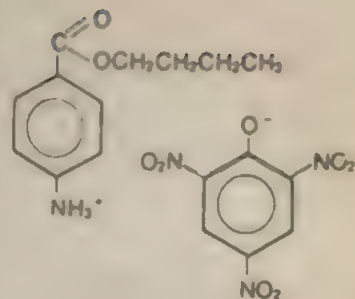
More powerful than procaine—but also more toxic—is the compound butacaine. Another chemical, tetracaine, is used for topical anesthesia of the eyes and for spinal anesthesia. The local of choice nowadays is usually lidocaine. This compound is highly effective and yet has a fairly low toxicity (table 23.2). Note that lidocaine is not a derivative of *p*-aminobenzoic acid. It does share some structural features with the other compounds, however.

Table 23.2
Toxicities of a variety of drugs*

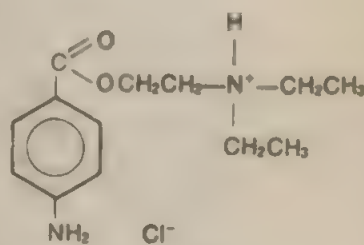
		<i>LD₅₀ (in milligrams per kilogram of body weight)</i>	<i>Method of Administration</i>	<i>Experimental Animal</i>
Local anesthetics	Lidocaine	400	Subcutaneous	Mice
	Procaine	50	Intravenous	Rats
	Cocaine	17.5	Intravenous	Rats
Barbiturates	Barbital	600	Oral	Mice
	Pentobarbital	130	Intraperitoneal	Mice
	Secobarbital	125 (MLD)†	Oral	Rats
	Phenobarbital	660	Oral	Rats
	Amobarbital	575	Oral	Rabbits
	Thiopental	120	Intraperitoneal	Rats
Narcotics	Morphine	500	Subcutaneous	Mice
	Codeine	120 (MLD)	Oral	Guinea pigs
	Heroin	150	Subcutaneous	Rabbits
	Meperidine	170	Oral	Rats
Stimulants	Caffeine	200	Oral	Rats
	Nicotine	55	Oral	Rats
		1.0 (MLD)	Intravenous	Rats
	Amphetamine	5 (MLD)	Oral	Rats
		85	Oral	Rabbits
	Methamphetamine	70	Intraperitoneal	Mice
	Epinephrine	50	Oral	Mice
	Mescaline	500	Intraperitoneal	Mice

*Comparisons of toxicities in different animals—and extrapolation to humans—are at best crude approximations. Method of administration can also have a profound effect on the observed toxicity.

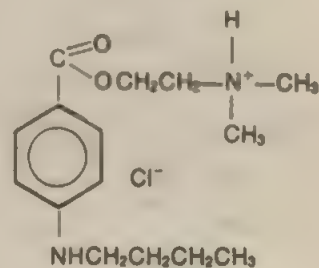
†Minimum lethal dose.



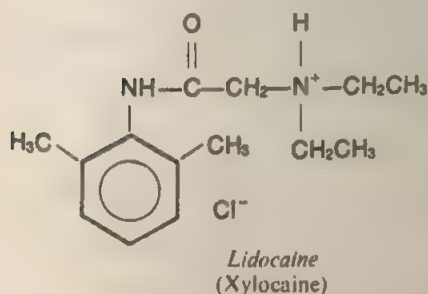
Butesin Picrate



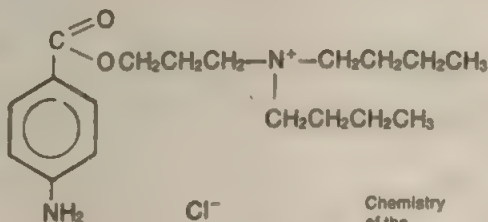
Procaine
(Novocaine)



Tetracaine



Lidocaine
(Xylocaine)

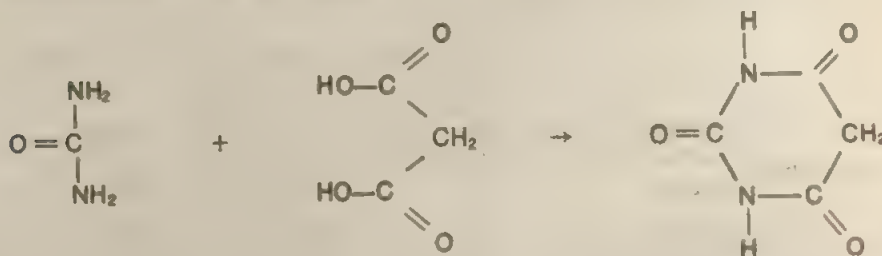


Butacaine

The Barbiturates: Sedation, Sleep, and Suicide

As a family of related compounds, the barbiturates display a wide variety of properties. They can be employed to produce mild sedation, deep sleep, and even death.

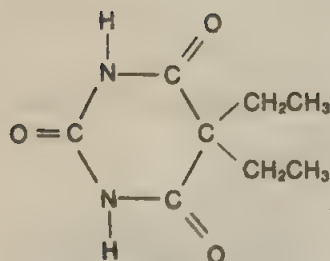
Barbituric acid was first synthesized in 1864 by Adolph von Baeyer, a young student of August Kekulé (chapter 10). He made it from urea, which occurs in urine, and malonic acid, which occurs in apples. The term *barbiturates*, according to Willstätter, came about because, at the time of the discovery, von Baeyer was infatuated with a girl named Barbara. The word comes from *Barbara* and *urea*.



The medicinal value of the barbiturates was discovered in 1903 by Joseph von Mering. A derivative, called barbitol, was found to be useful in putting dogs to sleep. Several thousand barbiturates have been synthesized through the years, but only a few have found widespread use in medicine. Pentobarbital (*Nembutal*) is employed as a short-acting hypnotic drug. Before the discovery of the modern tranquilizers, pentobarbital was used widely to calm anxiety and other disorders of psychic origin.

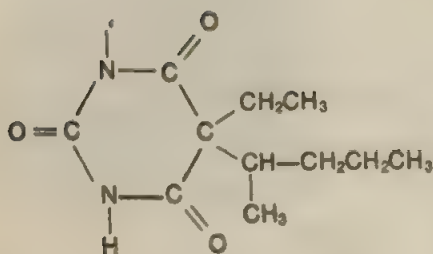
Another short-acting barbiturate is secobarbital (*Seconal*). It is used as an hypnotic and a sedative. Phenobarbital (*Luminal*) is a long-acting drug. It, too, is an hypnotic and can be used as a sedative. Phenobarbital is employed widely as an anticonvulsant for epileptics and brain-damaged people. The action of amobarbital (*Amytal*) is intermediate in duration.

Thiopental* (*Pentothal*), a compound that differs from pentobarbital only in that an oxygen atom on the ring has been replaced by a sulfur atom, is used widely in anesthesia (see p. 338).

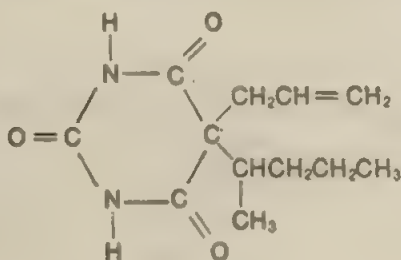


Barbitol
Veronal

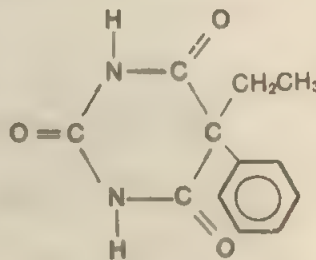
*Thiopental has been investigated as a possible truth drug. It does seem to help psychiatric patients recall traumatic experiences. It also helps uncommunicative individuals talk more freely. It does not, however, prevent one from withholding the truth or even from lying. No true truth drug exists.



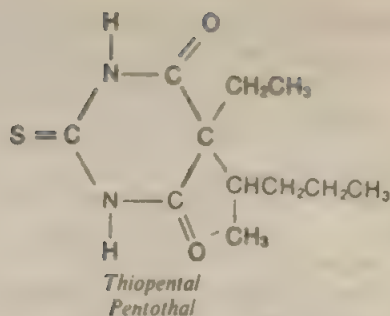
Pentobarbital
Nembutal



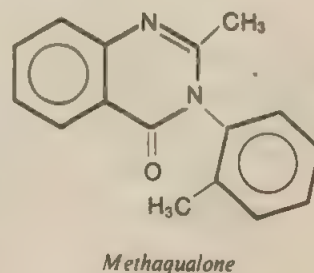
Secobarbital
(Seconal)



Phenobarbital
Luminal



In the 1970's, methaqualone (*Quaalude*, *Soper*, *Parest*) became a popular item on the illegal drug scene. Although it's not a barbiturate, it also acts as a sedative and an



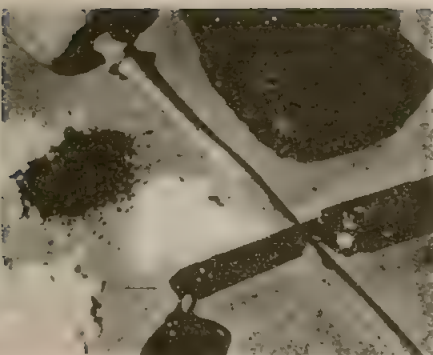
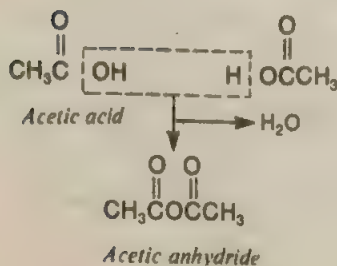
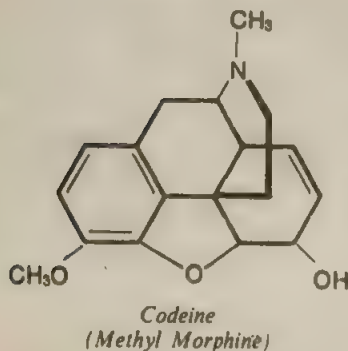
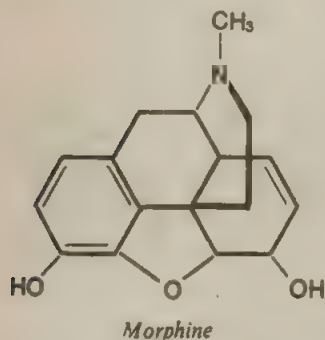


Figure 23.5 Opium poppy and derivatives: crude and smoking opium, codeine, heroin, and morphine. (Courtesy of the Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)



hypnotic. (Note that the middle ring in the molecule has the same atoms, in the same order, as the barbiturates; this structural feature may account for its action.)

Methaqualone was known to have the potential to produce dependence and tolerance in a steady user. Supposedly, it was available only by prescription, but the drug was not restricted as a narcotic. Vast quantities were diverted into illegal channels. Widespread use soon revealed the true nature of methaqualone. It was found to be strongly addictive, with withdrawal symptoms worse than those of heroin. Tolerance developed rapidly, often taking only a few days. A deadly synergism with alcohol was noted. After the extent of the problem became widely known, the Food and Drug Administration moved rapidly in 1973 to control the production and use of the drug.

Methaqualone faded somewhat from the illegal scene, only to achieve new notoriety in 1977 when a popular television actor shot himself while in a state of deep depression. He had been taking large doses of methaqualone, a depressant.

The Opium Alkaloids: Narcotics

Narcotics are drugs that produce narcosis (stupor or general anesthesia) and relief of pain (analgesia). Many drugs produce these effects, but in the United States only those that are also *addictive* are legally classified as narcotics. Their use is regulated by Federal law.

Opium is the dried resinous juice of the unripe seeds of the oriental poppy (*Papaver somniferum*). It is a complex mixture of some 20 nitrogen-containing organic bases (alkaloids), sugars, resins, waxes, and water. The principal alkaloid, **morphine**, makes up about 10% of the weight of raw opium.

Raw opium was used in many of the patent medicines of the nineteenth century. Ayer's Cherry Pectoral, Jayne's Expectorant, Pierce's Golden Medical Discovery, and Mrs. Winslow's Soothing Syrup were but a few of the many such products.

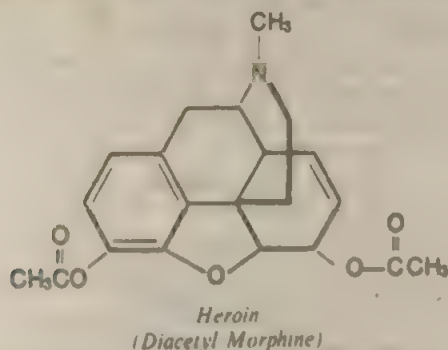
Morphine was first isolated in 1805 by Frederick Sertürner, a German pharmacist. With the invention of the hypodermic syringe in the 1850s, a new method of administration became available. Injection of morphine directly into the bloodstream was more effective for the relief of pain, but it also seriously escalated the problem of addiction. Morphine was used widely during the American Civil War (1860-1865). It was effective for relief of pain caused by battle wounds. One side effect of morphine use is constipation. Noting this, soldiers came to use morphine as a treatment for that other common malady of men on the battle front—dysentery. During their wartime service, over a hundred thousand soldiers became addicted to morphine. The affliction was so common among veterans that it came to be known as "soldier's disease."

Morphine and other narcotics were placed under the federal government's control by the Harrison Act of 1914. Morphine is still used by prescription for relief of severe pain. It also induces lethargy, drowsiness, confusion, euphoria, chronic constipation, and depression of the respiratory system. It is strongly addictive if administered in amounts greater than the prescribed doses or for a period longer than the prescribed time.

Slight changes in the molecular architecture of morphine produce altered physiological properties. Replacement of one of the —OH groups by an —OCH₃ group produces codeine. Actually, codeine occurs in opium to an extent of about 0.5%. It is usually synthesized, however, by methylating the more abundant morphine molecules.

Codeine is similar to morphine in its physiological action except that it is less potent and has less tendency to induce sleep. It is also thought to be less addictive. In

amounts of less than 1 grain per fluid ounce (2.2 mg per millilitre). codeine is exempt from the stringent narcotics regulations and is used in cough syrups.



In the laboratory, reaction of morphine with acetic anhydride (acetic anhydride is derived from acetic acid by removal of water) produces heroin. This morphine derivative was first prepared by chemists at the Bayer Company of Germany in 1874. It received little attention until 1890, when it was proposed as an antidote for morphine addiction! Shortly thereafter, Bayer was widely advertising heroin as a sedative for coughs, often in the same ads as aspirin. However, it soon was found that heroin induced addiction more quickly than morphine and that heroin addiction was harder to cure.



Figure 23.7 An old-fashioned hypodermic syringe. (Courtesy of the Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

The physiological action of heroin is similar to that of morphine except that it seems to produce a stronger feeling of euphoria for a longer period of time. Heroin is so strongly addictive that often only one or two injections are sufficient to induce dependence in some individuals. Heroin is not legal in the United States, even by prescription. It has, however, been advocated for use in relief of pain in terminal cancer patients and has been so used in Britain.

Addiction probably has three components: (1) emotional dependence, (2) physical dependence, and (3) tolerance. Psychological dependence is evident in the

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40 Stone Street, New York.



Figure 23.6 Trade card advertising Mrs. Winslow's soothing syrup. (Courtesy of the Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

Figure 23.8 Heroin was advocated as a safe medicine in 1900. It was widely marketed as a sedative for coughs. (Courtesy of the Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)



Figure 23.9 Street heroin. (Courtesy of the Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)



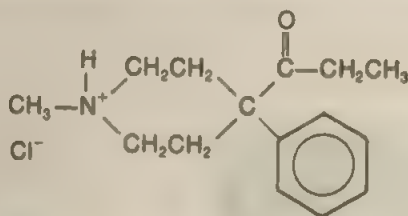
Figure 23.10 Forms of meperidine, a synthetic narcotic. (Courtesy of the Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

uncontrollable desire for the drug. Physical dependence is shown by acute withdrawal symptoms, such as convulsions. The body cells are conditioned to the drug and cannot function normally without it. The difference in physical and psychological dependence may be only one of degree, not kind. Both are likely to be biochemical in origin. Tolerance for the drug is evidenced by the increasing dosages required to produce in the addict the same degree of narcosis and analgesia.

Deaths from heroin usually are attributed to overdoses, but the situation is not altogether clear. The problem seems to be a matter of quality control. As an illustration, the office of the chief medical examiner for New York City analyzed 132 samples of drugs, supposedly heroin, that had been confiscated on the streets. Twelve contained no heroin at all. The remaining 120 varied from 1% to 77% heroin. A user could think he or she was getting a dose of 1 unit, when he or she was actually getting 77 times as much—a catastrophic overdose.

Synthetic Narcotics: Analgesia and Addiction

Much research has gone into attempts to develop a drug that would be as effective as morphine for the relief of pain but that would not be addictive. Perhaps the best known of the synthetic narcotics is meperidine (*Demerol*). Meperidine is somewhat less effective than morphine, but it has the advantage that it does not cause nausea. Repeated use, unfortunately, does lead to addiction.



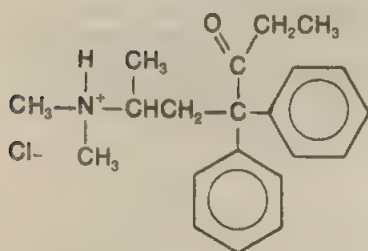
Meperidine (Demerol)

Another synthetic narcotic is methadone. This drug has been used widely to treat heroin addiction. Like heroin, methadone is highly addictive. However, when taken orally, it does not induce the sleepy stupor characteristic of heroin intoxication. Unlike a heroin addict, a person on methadone maintenance usually is able to hold a productive job. Methadone is available free in clinics. If an addict who has been taking methadone reverts to heroin, the methadone in his or her system effectively blocks the euphoric rush normally given by heroin, and so reduces the addict's temptation to use heroin.

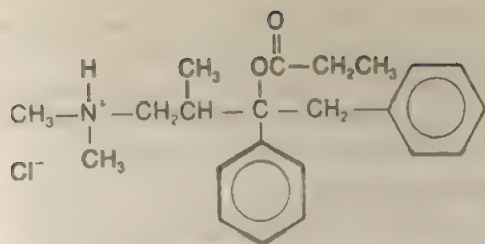
Methadone maintenance is not a perfect answer. Perhaps it is not even a good one. When injected into the body, methadone gives an effect similar to that of heroin, and methadone has been diverted for illegal use in this manner. And an addict on methadone is still an addict. All the problems of tolerance (and cross-tolerance with heroin and morphine) still exist.

Still another synthetic narcotic is propoxyphene hydrochloride (*Darvon*). This drug has been used widely as a prescription pain reliever. Independent studies (reference 15) have shown that *Darvon* is no more effective than aspirin for the relief of pain. Structurally, *Darvon* is quite similar to meperidine and methadone. Recently, it also has been shown to be addictive.

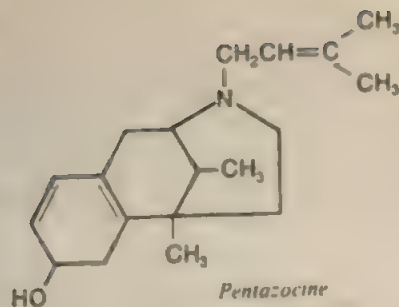
Chemists have synthesized thousands of morphine analogs. Only a few have shown significant analgesic activity. Most are addictive. Morphine acts by binding to receptors in the brain. Those molecules that have morphinelike action are called *agonists*. Morphine *antagonists* are drugs that block the action of morphine, most



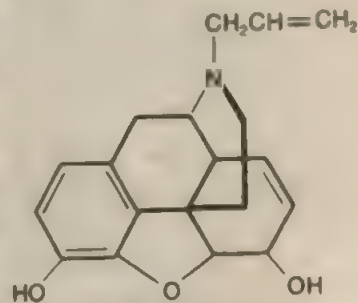
Methadone



Propoxyphene hydrochloride
(Darvon)



Pentazocine
(Talwin)



Naloxone

likely by blocking the receptors. Some molecules have both agonist and antagonist activity. These show great promise as analgesics. An example is pentazocine (*Talwin*). It is less addictive than morphine and yet it is effective for relief of pain. There is some hope that an effective analgesic could be developed that is not addictive, but to date the two effects seem inseparable.

Pure antagonists such as naloxone are of value in treating opiate addicts. Overdosed addicts can be brought back from death's door by an injection with naloxone. Long acting antagonists can block the action of heroin for as much as a month, thus aiding an addict in overcoming his or her addiction.

A Natural High: The Brain's Own Opiates

Morphine acts by fitting specific receptor sites in the brain. These morphine receptors were first demonstrated in 1973 by Solomon Snyder and Candace Pert at Johns Hopkins University School of Medicine.

Why should the human brain have receptors for a plant-derived drug like morphine? There seemed to be no good reason, so several investigators started a search for morphine-like substances produced by the human body. Not one but several such substances soon were found. Each was a short *peptide* chain, composed of amino acid units. Those with 5 amino acid units are called *enkephalins*. Those with 30 amino acid units are called *endorphins*. Both seem to be derived from a pituitary peptide called β -lipotropin.

Some of the enkephalins have been synthesized and shown to be potent pain relievers. Their use in medicine is quite limited, however, because, after being injected, they are rapidly broken down by the enzymes that hydrolyze proteins. It is hoped, though, that analogs more resistant to hydrolysis can be employed as morphine substitutes for the relief of pain. Unfortunately, both the natural enkephalins and the analogs, like morphine, seem to be addictive.

It appears that enkephalins and endorphins are released as a response to pain deep in the body. Bruce Pomeranz of the University of Toronto has collected evidence that indicates that acupuncture anesthetizes by stimulating the release of the brain "opiates." The long needles stimulate deep sensory nerves that cause the release of the peptides that then block the pain signals.

Endorphin and enkephalin release also has been used to explain other phenomena once thought to be largely psychological. A soldier, wounded in battle, feels no pain until the skirmish is over. His body has secreted its own pain killer. Similarly, an athlete can perform with an injury and not feel pain until the contest is over.

Deep sensory nerves, stimulated by vigorous exercise, trigger the release of endorphins, which block the pain message. Long-distance runners experience many of the symptoms that opiate users do. They get euphoric highs during or after a hard

run. They also suffer from withdrawal; they feel bad when they don't get the vigorous exercise of a long, hard run.

Do you want a good, cheap, legal high? Get yourself in good physical condition and take part in some vigorous exercise. Your body will produce its own "opiates." Be forewarned, however. You may get hooked on exercise.

The Stimulants: Up, Up and Away

Just as there is a wide variety of downers, there is an array of stimulant drugs. Along with the depressants, many of these are derived from plants. Caffeine, a mild stimulant, generally is consumed in beverages made from coffee beans, tea leaves, and cola nuts. The effective dose of caffeine is about 200 mg, corresponding to about two cups of strong coffee or tea. Caffeine is also available in tablet form as a stay-awake or keep-alert type of drug. The best known brands are probably *No-Doz* and *Vivarin*. *No-Doz* contains about 100 mg of caffeine per tablet, and each *Vivarin* tablet has 200 mg.

Is caffeine addictive? The "morning grouch" syndrome indicates that it may be mildly so. There is also evidence that caffeine may be involved in chromosome damage. To be safe, young people in their childbearing years should avoid large quantities of caffeine. Overall, the hazards of caffeine ingestion seem to be slight.

Going Up in Smoke: Nicotine Addiction

Another common stimulant is nicotine. This drug is taken by the smoking of tobacco. Nicotine is highly toxic to animals (table 23.2). It is especially deadly when injected; the lethal dose for a human is estimated to be about 50 mg. Nicotine is used widely in agriculture as a contact insecticide.

Nicotine seems to have a rather transient effect as a stimulant. This initial response is followed by depression.

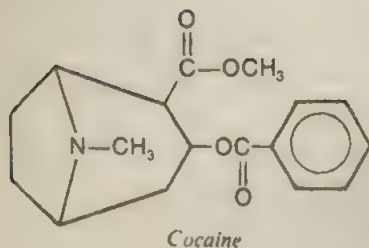
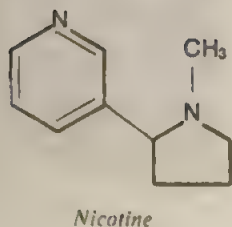
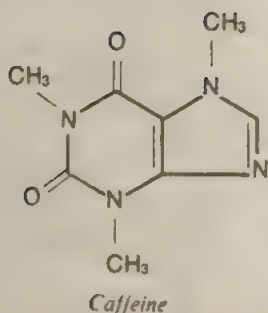
Is nicotine addictive? Casual observation of a person who is trying to quit smoking seems to indicate that it is. There is also evidence of the development of tolerance. It is difficult, however, to separate all the social factors involved in smoking from the physiological effects.

Cocaine: The Snow Sniffers

Cocaine, mentioned earlier as a local anesthetic, also serves as a powerful stimulant. Cocaine is obtained from the leaves of a shrub that grows almost exclusively on the eastern slopes of the Andes Mountains. Many of the Indians living in and around the area of cultivation chew the leaves—mixed with lime and ashes—for their stimulant effect. Cocaine usually arrives in the United States in glistening white crystals; hence the slang name "snow." Some cocaine is legally imported for legitimate human and veterinary medical purposes. A far greater quantity is smuggled in for the illegal drug market.

Cocaine stimulates mental activity and quickens the reflexes. It increases stamina and reduces fatigue. Moreover, it gives the user a feeling of confidence and power. It induces euphoria in some users. These stimulant effects are short-lived (about 1 hour) and are followed by depression. Overdose or repeated use can lead to paranoia, psychosis, and hallucinations. Overdose can cause death through heart attack or respiratory arrest.

Cocaine is expensive. It is popular among wealthy international socialites, the "jet-set." These people usually sniff it up their noses from specially designed spoons. Repeated administration in this manner leads to a deterioration of the mucous linings of the nose. The snorter thus is rendered more susceptible to infection and disease.

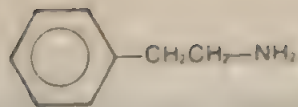


Lower-Class Uppers: The Amphetamines

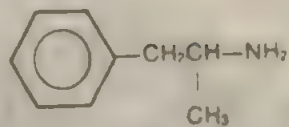
A variety of amines, related to *o*-phenylethylamine, act as stimulants. As a class, these compounds are called amphetamines, after the simplest member of the group. Two of these amines, amphetamine and methamphetamine, have been abused widely. Amphetamines also have been prescribed for weight reduction. They are used for treating mild depression and narcolepsy, a rare form of epilepsy that is characterized by sudden sleepiness.

Amphetamines induce excitability, restlessness, tremors, insomnia, dilated pupils, increased pulse rate and blood pressure, hallucinations, and psychoses. Amphetamines are no longer recommended for weight reduction. Any weight loss resulting from their use was generally only temporary. The greatest problem, however, was the diversion of vast quantities of amphetamines into the illegal drug market. Amphetamines are inexpensive. Armed forces personnel, truck drivers, and college students have been among the heavy users. Some of the slang names originated among truck drivers, who called them "coast-to-coasts" and "copilots." They also are called "bennies," "pep pills," and by a variety of names descriptive of the shape or color of the pills, such as "peaches," "roses," and "hearts."

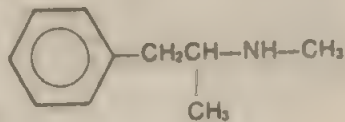
Methamphetamine has a more pronounced psychological effect than amphetamine. Generally, the "speed" that abusers inject into their veins is methamphetamine. Such injections, at least initially, are said to give the abuser a euphoric



o-Phenylethylamine



Amphetamine
(Benzedrine)



Methamphetamine
(Methedrine)

Dextroamphetamine (*Dexedrine*) is another stimulant drug that has been abused widely. It is structurally related to amphetamine in a very subtle way. Actually, amphetamine is not a single compound but a mixture of two isomers. These isomers have the same atoms and same groups of atoms, but the relative spatial orientations of these constituent atoms and groups are different in the two isomers. One isomer is the mirror image of the other.



These isomers are not superimposable but are related to one another in much the same way that your right hand is related to your left. You can't fit a right-hand glove on your left hand or vice versa. These mirror-image isomers fit enzymes differently; thus they have different effects. The dextro ("right-handed") isomer is a stronger stimulant than the levo ("left-handed"). *Dexedrine* is the trade name for the pure dextro isomer. *Benzedrine* is the trade name for a mixture of the two isomers in equal amounts. *Dexedrine* is two to four times as active as *Benzedrine*.

Mirror-image isomerism is quite common in organic chemicals of biological importance. Usually only one of the two isomers occurs in nature; thus, for many purposes, it is not necessary to emphasize the isomerism. However, any molecule that has four different groups attached to a single carbon atom can exist as mirror-image isomers. Lactic acid is a familiar example.



The dextro isomer occurs in blood and muscle tissue, where it is formed by the oxidation of glucose. Levo lactic acid occurs in sour milk.

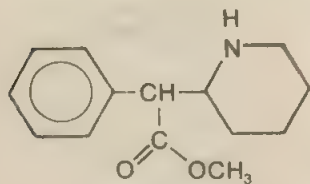


Figure 23.11 A *Bensedrine* inhaler, 1932. Abuse led to the banning of the inhaler. (Courtesy of the Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

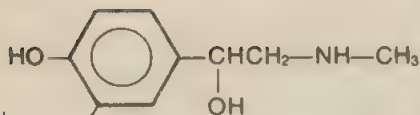


Figure 23.12 Amphetamine tablets (Courtesy of the Bureau of Narcotics and Dangerous Drugs, Washington D.C.)

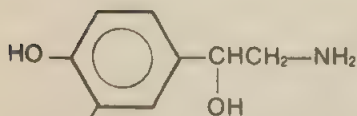
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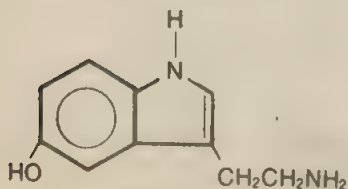
Methylphenidate
(Ritalin)



Epinephrine
"Adrenalin"



Norepinephrine



Serotonin

rush. Shooting methamphetamine is quite dangerous, though, and the drug is rather toxic (table 23.2).

One highly controversial use of amphetamines has been their employment in the treatment of hyperactivity in children. The drug of choice is often methylphenidate (*Ritalin*). Although it is a stimulant, the drug seems to calm kids who otherwise can't sit still. This use has been criticized as "leading to drug abuse" and as "solving the teacher's problem, not the kid's."

Brain Amines: The Ups and Downs of Life

We all have our ups and downs in life. Recent attempts have been made to quantify these as biological rhythms (references 19 and 20). Women seem to go through emotional states closely related to the menstrual cycle, with highs occurring in the early part of the cycle and depression deepening toward the onset of menses. These subjective emotional states may well be related to the flow of female sex hormones (chapter 22). Surprisingly, perhaps, men also seem to go through monthly cycles. These may be related to the secretion of certain adrenal steroids.

Certain other hormones also may be involved. One well-known compound, epinephrine, commonly called ~~adrenalin~~ *adrenalin*, is secreted by the adrenal glands. A tiny amount of epinephrine causes a great increase in blood pressure. When a person is under stress or is frightened, the flow of adrenalin prepares the body for fight or flight. Because culturally imposed inhibitions prevent fighting or fleeing in most modern situations, the adrenalin-induced supercharge is not used. This sort of frustration has been implicated in some forms of mental illness.

One widely held theory (of a biochemical basis) about mental illness involves a relative of epinephrine—norepinephrine—and another hormone—serotonin. Whereas norepinephrine, like epinephrine, is a powerful stimulant, serotonin is a depressant. A normal mental condition involves a delicate balance of the two compounds in the brain. When something happens in the biochemistry of the body, to cause an excess of serotonin in the brain, a person becomes depressed. The greater the excess, the greater the depression. If, on the other hand, norepinephrine is formed in excess, the person is in an elated, perhaps hyperactive state. In large excess, norepinephrine could cause a *manic* state.

Richard Wurtman of the Massachusetts Institute of Technology has found a relationship between diet and serotonin levels in the brain. Serotonin is produced in the body from the amino acid tryptophan (figure 23.13). The synthesis involves

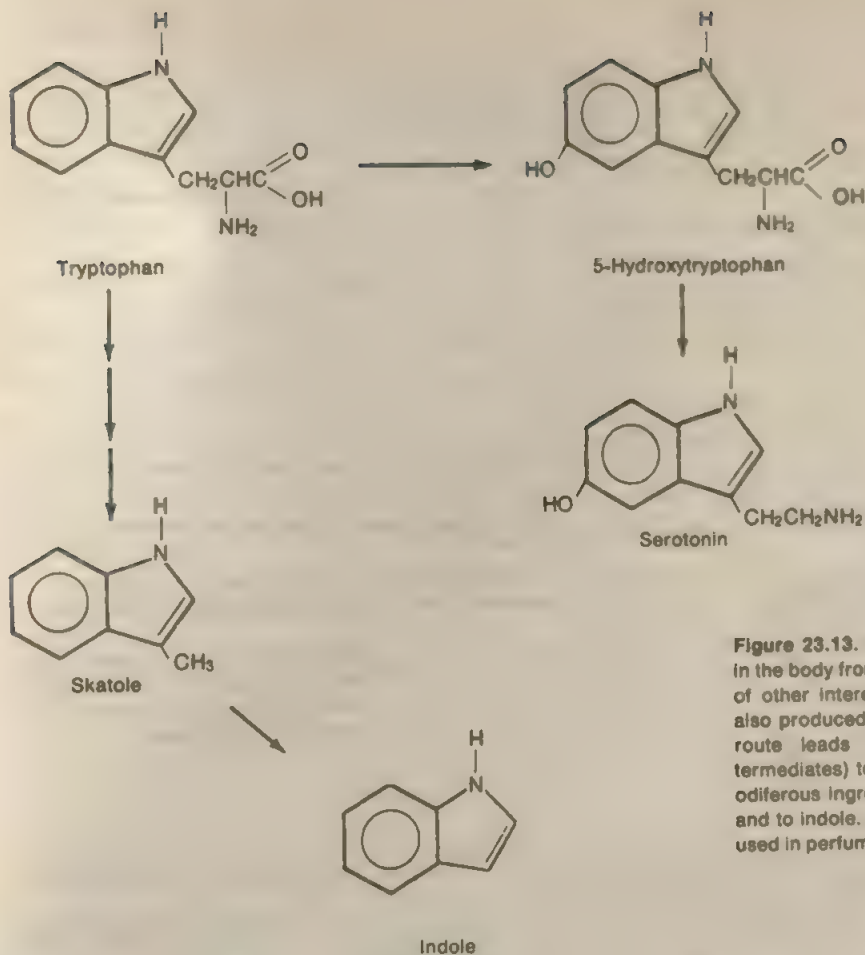


Figure 23.13. Serotonin is produced in the body from tryptophan. A variety of other interesting compounds are also produced from tryptophan. One route leads (through several intermediates) to skatole, the principal odiferous ingredient in human feces, and to indole. Skatole and indole are used in perfumes (chapter 20).

several steps, each catalyzed by an enzyme. Wurtman found that diets high in carbohydrates lead to high levels of serotonin. Lots of protein lowers the serotonin concentration. That may seem strange because protein has lots of tryptophan and carbohydrate foods have little. But, Wurtman says, protein is only 1% tryptophan. In the presence of all those other amino acids, little tryptophan reaches the brain. With a carbohydrate meal, the hormone *insulin* lowers the level of the other amino acids in the blood, allowing relatively high levels of tryptophan to reach the brain.

Norepinephrine also is synthesized in the body from an amino acid. It is derived from tyrosine. The synthesis is complex and proceeds through several intermediates (figure 23.14). Each step is catalyzed by one or more enzymes. The intermediate compounds also have physiological activity. Dopa has been used successfully in the treatment of Parkinson's disease. Dopamine has been employed to treat low blood pressure. Since tyrosine is also a component of our diets, it may well be that our mental state depends to a fair degree on our diet.

Before leaving this section, note the similarity in structure of the natural uppers—epinephrine and norepinephrine—and the synthetic ones—amphetamine and methamphetamine. All are derived from the basic β -phenylethylamine structure. Perhaps the amphetamines act as stimulants by mimicking the natural brain amines.

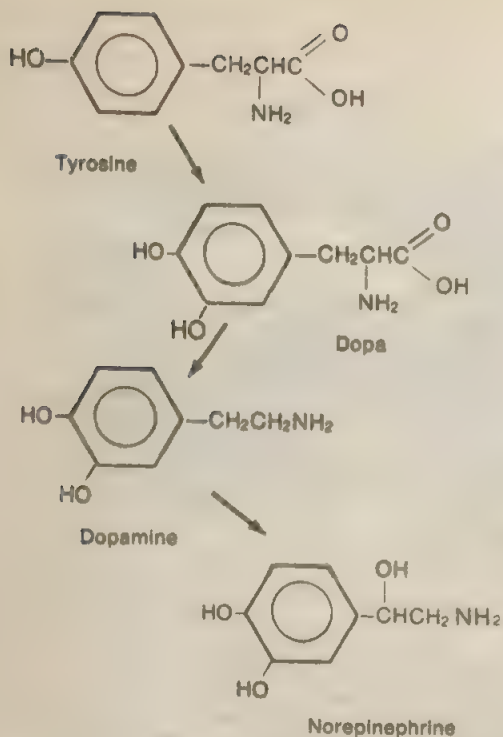


Figure 23.14 The biosynthesis of norepinephrine from tyrosine.

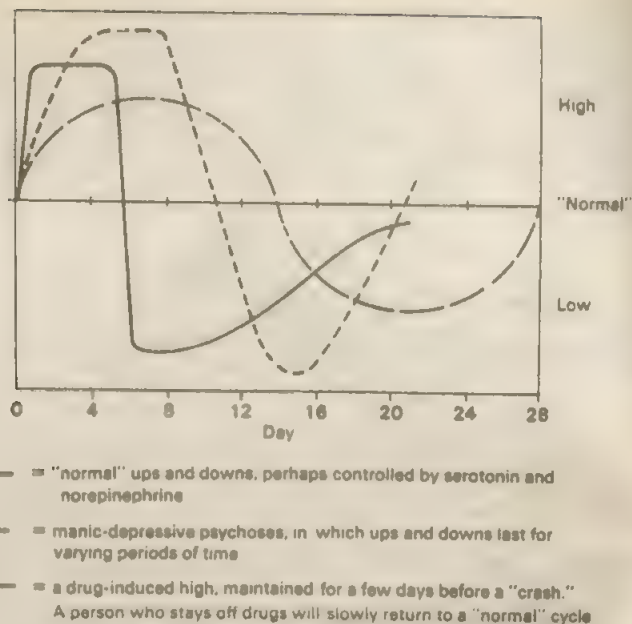


Figure 23.15 Effects of drugs on the mental state of an individual. The diagram is illustrative only and should not be interpreted literally.

(No such structural relationships are apparent between serotonin and the synthetic downers, such as the barbiturates.)

We can readily see how the use of drugs would affect mental cycles. Chemicals can be used to induce artificial highs and lows (figure 23.15). Achieving an artificial high (with amphetamines or cocaine, for example) is not without its risks, however. When people come down from a chemical high, they don't just return to normal. They "crash" into an abnormal low—a deep, often suicidal, depression. To avoid the crash, a user often will take more of the drug to try to maintain the high. The body develops a tolerance to most drugs, however, and ever larger doses are necessary. Such a buildup can lead to dangerously toxic levels—and to psychoses. Other addicts use barbiturates to come down quickly and to get to sleep. After sleeping, they feel groggy and take an upper to help them get going. Hooked on a chemical seesaw, these unfortunate people usually come quickly to grief.

Drugs are used medically to regulate abnormal highs and lows such as those that occur in manic-depressive psychoses. Lithium carbonate (Li_2CO_3) has been approved for use in leveling out the dangerous manic stage. Psychic energizers such as imipramine (p. 352) can be used to combat deep depression.

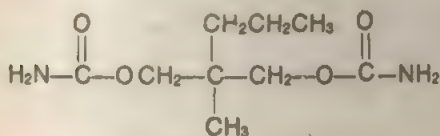
It has been estimated that nearly 1 out of every 10 people in the United States suffers from mental illness. Over half the patients in hospitals are there because of mental problems. When the biochemistry of the brain is more fully understood, mental illness may be cured (or at least alleviated) by administration of drugs. In the remainder of this chapter, we see just how far we have already come in learning to control our moods with drugs. As is true for so many things, the potential for good that such compounds represent is matched by a potential for abuse.

Chemical Quiet: The Tranquillizers

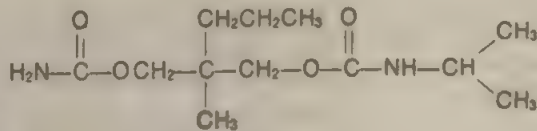
The hectic pace of life in the United States has driven people to seek rest and relaxation in chemicals. Ethyl alcohol is undoubtedly the most widely used tranquilizer. The drink before dinner—to unwind from the tensions of the day—is very much a part of the American way of life. However, some people seek relief through the use of other chemicals.

Several over-the-counter drugs (such as *Cope*, *Vanquish*, *Compoz*, and *Quiet World*) claim to be able to help us cope with, or vanquish, our problems, or at least to compose ourselves in the face of minor adversity. Such products usually contain a little aspirin plus an antihistamine. The latter has a side effect of drowsiness. Such products have come under attack by consumer groups for being worthless at best and perhaps even dangerous.

Another group of drugs, available only by prescription, is employed to calm nervous tension. Several of these are carbamates. Simple derivatives, such as ethyl carbamate, act as mild soporifics (sleep-inducing agents). The best-known tranquilizer in this group is meprobamate (*Equanil* and *Miltown*). Sales amount to tens of millions of dollars per year. Another carbamate, carisoprodol (*Soma*) is prescribed as a muscle relaxant.



Meprobamate
(*Equanil* or *Miltown*)



Carisoprodol
(*Soma*)

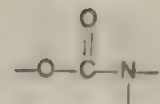
Two other widely used antianxiety drugs have seven-membered heterocyclic rings. They are diazepam (*Valium*) and chlorodiazepoxide (*Librium*). These benzodiazepine derivatives and the carbamates were formerly called "minor tranquilizers." Extensive studies of the effects of these drugs have revealed contradictory results. Some studies have shown them to be remarkably effective. Others have found the drugs to be little better than a placebo. All the results show that, to a remarkable degree, the results depend upon the expectations of the patients.

Despite the uncertainty concerning their effectiveness and recent evidence that these, too, are addictive drugs, they remain in widespread use. *Valium* was the most prescribed brand-name drug in the United States in 1977. *Librium* was eighth on the list.

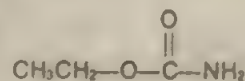
Antipsychotic Drugs: Emptying the Mental Hospitals

For centuries, the people of India used the snakeroot plant, *Rauwolfia serpentina*, to treat a variety of ailments, including fever, snakebite and other poisonings, and—most important—maniacal forms of mental illness. Western scientists became interested in the plant near the middle of the twentieth century—after disdaining such remedies as quackeries for many generations.

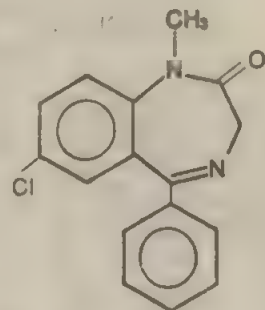
In 1952, rauwolfia was introduced into American medical practice as a hypotensive (blood-pressure-reducing) agent by Robert Wilkins of Massachusetts General Hospital. In the same year, Emil Schlittler of Switzerland isolated an active alkaloid, which he named reserpine. The plant extract was found to reduce blood pressure and bring about sedation. The latter finding attracted the interest of psychiatrists, who found reserpine so effective that by 1953 it had replaced electroshock therapy in the treatment of 90% of their psychotic patients.



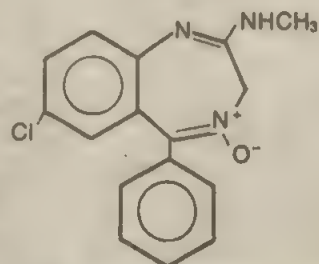
The carbamate functional group



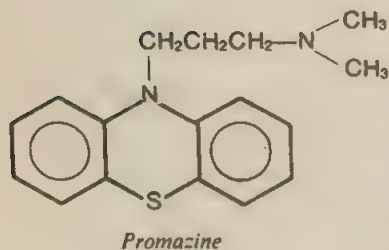
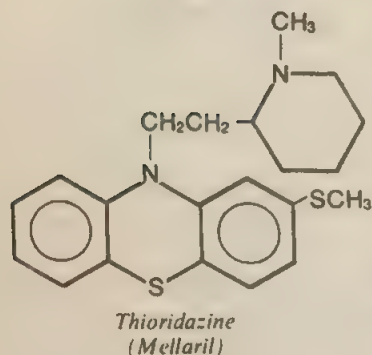
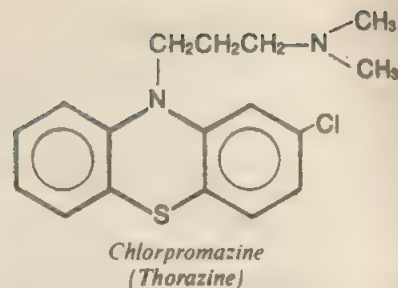
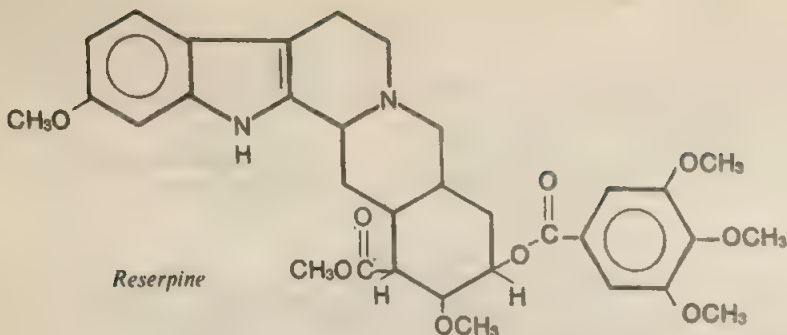
Ethyl Carbamate
(a mild soporific)



Diazepam
(*Valium*)



Chlordiazepoxide
(*Librium*)



Also in 1952, chlorpromazine (*Thorazine*), which had been used in France as an antihistamine, was tried on psychotic patients in the United States as a tranquilizer. It was found to be extremely effective for treating the symptoms of schizophrenia.

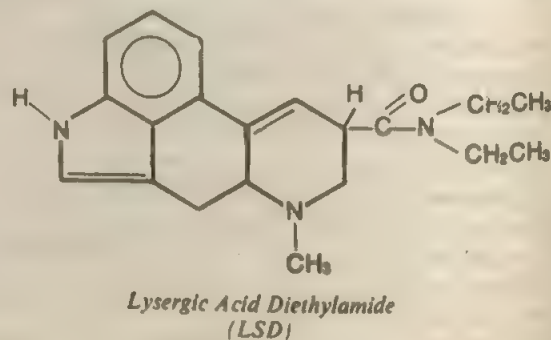
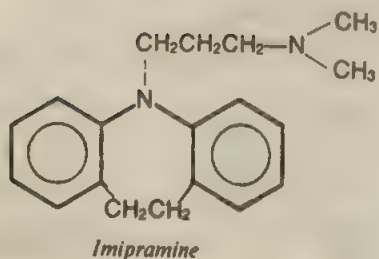
Many compounds related to chlorpromazine have been synthesized. Several of these have been found to have interesting physiological properties. Promazine itself is a tranquilizer, but it's not as potent as chlorpromazine. Thioridazine (*Mellaril*) is a potent tranquilizer, reputed to be without some of the undesirable side effects of chlorpromazine.

It is of interest to note that imipramine, which differs from promazine only in that the sulfur atom is replaced by $-\text{CH}_2\text{CH}_2-$, is not a tranquilizer at all. Instead, it is a psychic energizer. This indicates that slight structural changes sometimes can result in profound changes in properties and that we have a long way to go in understanding why drugs act as they do.

The antipsychotic drugs—reserpine and the promazine derivatives—have been one of the real triumphs of chemical research. They have served to virtually empty the mental hospitals by controlling the symptoms of schizophrenia to the extent that 95% of all schizophrenics no longer need hospitalization. These drugs are not cures. Perhaps some day we will understand the causes of schizophrenia. At that time, perhaps a real cure—or a preventive—can be found.

The Mindbenders: LSD

The third major class of drugs is popularly called the "mindbenders" because they qualitatively change the way we perceive things. Probably the most powerful of these drugs is LSD (from the German *lysergsaure diethylamid*). The physiological properties of this compound were discovered quite accidentally by Albert Hofmann in 1943. Hofmann, a chemist at the Sandoz Laboratories in Switzerland, unintentionally ingested some LSD. He later took 250 μg , which he considered a small dose, to verify that LSD had caused the symptoms he had experienced. Hofmann had a very rough time for the next few hours, exhibiting such symptoms as visual disturbance and schizophrenic behavior.



Lysergic acid is obtained from ergot, a fungus that grows on rye. It is converted to the diethylamide by treatment with thionyl chloride (SOCl_2), followed by diethylamine.

LSD is a potent drug, as indicated by the small amount required for a person to experience its fantastic effects. The usual dosage is probably about 10 to 100 μg . No wonder Hofmann had a bad time with 250 μg ! To give you an idea of how small 10 μg is, let's compare that amount of LSD to the amount of aspirin in one tablet—one aspirin tablet contains about 300 000 μg of aspirin.

Is LSD a dangerous drug? A few facts are known, but most are disputed. In 1967, Malmon Cohen of the State University of New York at Buffalo reported that LSD damages chromosomes, especially those of the leucocytes (white blood cells). The report received wide publicity. Fear of damage to germ cells—and the subsequent birth of deformed babies—caused a decline in the use of LSD. Additional studies produced mixed results. Some seemed to confirm Cohen's findings. For example, in hamsters, LSD administered to pregnant females caused gross fetal deformities. Other studies, however, seemed to exonerate LSD as a cause of chromosomal damage. The question still has not been resolved.

Marijuana: Some Chemistry of Cannabis

Many complete books have been written about marijuana, yet all that is known for certain about the drug would fill only a few pages. Let's look at some chemistry of the weed and at some of the ways chemists are involved with the marijuana problem.

The weed *Cannabis sativa* has long been useful. The stems yield tough fibers for making ropes. *Cannabis* has been used as a drug in tribal religious rituals. Marijuana also has a long history as a medicine, particularly in India. In the United States, marijuana is second only to alcohol as an intoxicant.

The term *marijuana* refers to a preparation made by gathering the leaves, flowers, seeds, and small stems of the plant. These are generally dried and smoked. They contain a variety of chemical substances, many of them still unidentified. The principal active ingredient, however, has been identified as a tetrahydrocannabinol (THC).

Actually, there are several active cannabinoids in marijuana. Only one is shown here. Raphael Mechoulam of the Hebrew University was the first to isolate the active ingredient (1949). The compound was first synthesized in 1967.

Marijuana plants, as they grow in nature, vary considerably in THC content. Most of the marijuana sold in North America comes from Mexico and has a THC content of about 1%. That native to the United States has a low THC content, usually about 0.1%. Potency depends on the genetic variety of the plant, not to any significant extent on the climate or the soil where it is grown.

More potent preparations sometimes are made from marijuana. By selecting only the flowering tops and tender top leaves, you get a stronger product called ganja. (The ordinary marijuana is called *bhanga* in India.) Jamaican *ganja* has a THC content of between 4% and 8%. Indian ganja is generally somewhat less potent. By collecting only the resinous secretions of the flowering parts, you get a product called hashish (known as *charas* in India). Hash has a THC content of between 5% and 12%. Liquid hash and hash oil are probably solvent extracts of marijuana.

The effects of marijuana are difficult to measure, partly because of the variable THC content of different preparations. A variety of standard potency is now grown and supplied for controlled clinical studies. With this standard product, some of the effects of marijuana can be measured in reproducible experiments. Smoking *Cannabis* increases the pulse rate, distorts the sense of time, and impairs some

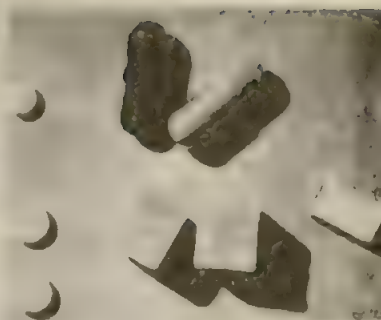


Figure 23.16 Illicit forms of lysergic acid diethylamide (LSD). (Courtesy of the Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

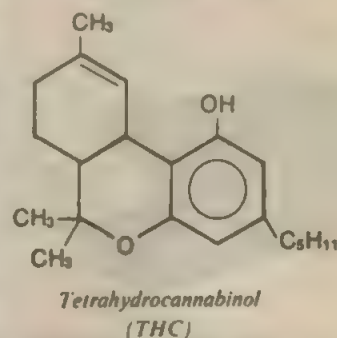


Figure 23.17 The marijuana plant. (Courtesy of Carolina Biological Supply Company.)

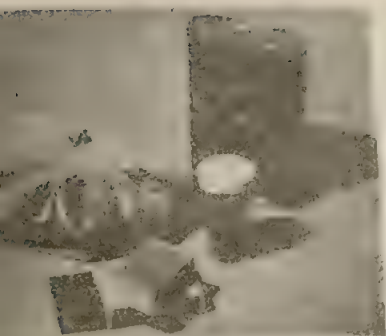


Figure 23.18 Retail forms of marijuana. (Courtesy of the Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

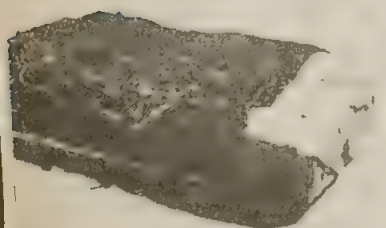


Figure 23.19 Marijuana dealers were early converts to the metric system. Shown here is a kilo brick of marijuana. (Courtesy of the Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)



Figure 23.20 Manicured marijuana, cigarettes, and seeds. (Courtesy of the Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

complex motor functions. These effects can be measured easily. Other results also have been noted widely, if less quantitatively. Marijuana smoking sometime induces a euphoric sense of lightness—a floating sensation. Sometimes it causes a feeling of anxiety. Often, the user has an impression of brilliance, although studies have shown no mind-expanding effects. Users sometimes experience hallucinations, although these are much less frequent than with LSD. Marijuana seems to heighten one's enjoyment of food, with users relishing beans as much as they normally would enjoy steak.

The long-term effects of marijuana use are more difficult to evaluate. Some people claim that smoking marijuana leads to the use of harder drugs. There is no objective evidence that this is the case. In fact, studies have shown that more heroin addicts started out on alcohol than on marijuana.

There is some evidence—both direct and indirect—that marijuana causes brain damage. In September 1971, it was announced that marijuana caused brain lesions in rats. Researchers in Great Britain associated laziness, passivity, and mental sluggishness with brain damage in young men who had been heavy smokers of marijuana. But there have been millions of users, and, even if the observed brain damage is due to marijuana, it is less extensive than that caused by alcohol.

Some people also have claimed that excessive use of marijuana leads to psychoses. It has long been known to induce short-term psychotic episodes in those already predisposed and in others who take excessive amounts. Long-term psychoses, however, occur at the same rate among regular marijuana users as among the general population.

One of the more interesting reports has come from two surgeons at the Harvard Medical School. Menelaos Athapoulis and John Harman claim to have treated 13 young men for gynecomastia—enlarged breasts. All were heavy marijuana users. Their breasts also discharged a white, milky liquid. The painful swelling receded in 3 of the men after they stopped smoking *Cannabis*, but 3 others needed surgery. The two doctors are convinced that marijuana contains a “feminizing ingredient.” There is a slight structural similarity of THC to the female hormones, and some studies have shown that THC bonds to estrogen receptors.

Chromosomal damage due to the use of marijuana also was reported during 1973. Morton A. Stenchever of the University of Utah reported nearly three times as many breaks in the chromosomes of users as in those of nonusers. Such breakage, if it occurs in germ cells, could result in birth defects. In other cells, it could cause cancer. Stenchever believes that the blame once placed on LSD as a chromosome breaker probably belongs to marijuana. All of the LSD users had been pot smokers, also.

What do chemists have to do with all this? Well, they have isolated the active components and synthesized them. They can monitor the THC content of marijuana. They can monitor THC in the bloodstream and identify the products of its breakdown. They cannot, however, tell how it changes the body chemistry or what its long-term effects are.

Perhaps the most significant harm from marijuana comes through its impairment of complex motor functions—such as those used in driving an automobile. In addition to dodging drunks, we have to look out for potheads. Incidentally, chemists have developed a THC detector similar to the one used to test blood alcohol. Let's hope the road is cleared of all intoxicated people, no matter what they are intoxicated with.

Unlike alcohol, THC persists in the bloodstream for several days, presumably because it is soluble in fats. The products of its breakdown remain in the blood for as long as 8 days.

The long persistence of these chemicals inside the body indicates that some of a given dose may still be active in the body at the time another dose is taken. This might account for the fact that an experienced pot smoker can get high on a dose that doesn't affect a novice.

Marijuana may well have some legitimate medical uses. It reduces pressure in the eyes of people who have glaucoma. If not treated, the buildup of pressure eventually causes blindness. Also, marijuana seems to relieve the nausea that afflicts cancer patients undergoing radiation treatment and chemotherapy.

Chemistry has the potential to reveal a great deal about the effects of marijuana. What we may learn may be unimportant, or it may be too late. It took us 300 years to find out that cigarette smoking can cause cancer and even longer to realize that alcohol is responsible for cirrhosis of the liver. We may be up against a third such toxic substance.

It does appear that, if the decision to legalize marijuana is made any time soon, it will most likely have to be made on something other than a scientific basis.

Drugs and Deception: Chemistry and Quality Control

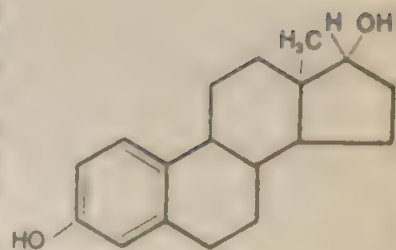
One recurring problem on the illegal drug scene is that drugs are not always what they are supposed to be. The buyers simply have to trust the sellers—and their own experience—about the identity and quality of the products they buy. Even with marijuana, a readily identified weed, there are problems of quality control. The nonpotent variety often is harvested and used to dilute the Mexican product to increase profits. The potent variety also may be cut with tea or other leaves for the same reason. The nonpotent variety also has been found to be laced with other drugs to produce some kind of physiological effect. Perhaps the most insidious additive was discovered in Northern Ireland. The marijuana was laced with opium in an attempt to turn a low-profit "grass" scene into a more lucrative heroin market.

Deception with other drugs is even more common. There have been numerous reports of synthetic THC on the illegal drug scene. Little if any has been confirmed by crime laboratories. Most "THC" has been shown to be either LSD or phencyclidine (PCP), an animal tranquilizer that has many adverse side effects in humans.

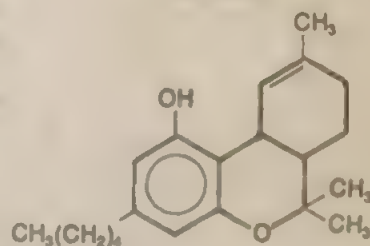
At times, PCP has become an important part of the illegal drug scene. It is cheap and easily prepared. Though it was ruled much too dangerous for human use, it is available as a tranquilizer for animals. Many users have experienced bad trips with PCP, but every few years a new crop of young people appears on the scene to be victimized by this hog tranquilizer. PCP is stored in the body fat, to be released to trigger recurrent bad trips days or weeks after the drug was first ingested.

Many fraudulent products frequent the illegal drug scene. The scare about chromosomal damage from LSD led to increased interest in mescaline, a drug derived from the peyote cactus. (Note that mescaline is another β -phenylethylamine.) Mescaline is scarce and expensive; yet a product called mescaline became readily available on the street in some areas. Lab analyses proved that the product was really PCP. In fact, crime labs generally have found nearly two-thirds of all drugs (other than marijuana) brought in for analysis to be something other than what the dealers said they were.

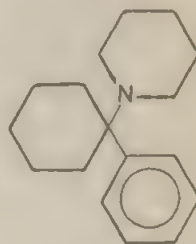
Chemistry can provide drugs of enormous benefit to society. It can provide drugs that present society with serious problems. But it can't solve the drug problem. However, chemistry can provide information on which intelligent choices can be based. The choices, though, are up to you, as an individual and as a member of society.



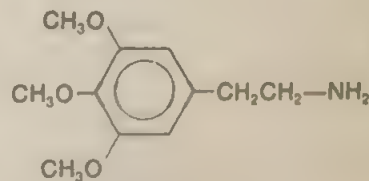
Estradiol



Tetrahydrocannabinol



*Phencyclidine
(PCP)*



Mescaline

Problems

- Which of the following drugs are pure chemical compounds? Which are mixtures?
 - heroin
 - marijuana
 - phenobarbital
 - opium
 - peyote
 - methadone
 - tetrahydrocannabinol
 - chlorpromazine
 - rauwolfia
 - phencyclidine
- Which of the drugs in question 1 occur in nature? Which are exclusively synthetic?
- Can people get high on alcohol? Explain your answer.
- Could the tendency toward alcoholism be inherited? Explain in terms of the liver enzyme cytochrome P-450.
- List three general anesthetics. What are the advantages and disadvantages of each?
- How does curare kill? How can such a deadly poison be used on people in surgery without killing them?
- How do local anesthetics work? What is spinal anesthesia?
- Refer to **table 23.2**. Which is more toxic, procaine or cocaine? Can you use the data in **table 23.2** to compare the toxicities of lidocaine and cocaine?
- Why is nicotine so much more toxic when injected intravenously than when taken orally?
- If the minimum lethal dose of amphetamine is 5 mg per kilogram, what would be the MLD for a 70-kg person? Can toxicity studies on animals always be extrapolated to humans?
- What is the basic structure common to all barbiturate molecules? How is the basic structure modified to change the properties of individual barbiturate drugs?
- What is synergism?
- What is the role of the chemist in the marijuana controversy?
- What are the three components of addiction? Can they be separated easily?
- How does methadone maintenance work? Do you think it is a good idea?
- Is caffeine addictive? Is nicotine?
- How does codeine differ from morphine in structure? In physiological effects?
- Are tranquilizers a cure for schizophrenia?
- Following are the generic names of several of the most widely prescribed drugs. Use *The Merck Index* or a similar reference to determine (if possible) the chemical structure, medical use, toxicity, and side effects of each.
 - fursemide
 - methyldopa
 - hydrochlorothiazide
 - digoxin
 - ibuprofen
 - flurazepam
 - propanolol
 - indomethacin
- What are some of the problems involved in the clinical evaluation of LSD?
- What are some of the problems in the clinical evaluation of marijuana?
- Is marijuana a narcotic legally? Clinically?
- How is heroin different from morphine?
- How are endorphins and enkephalins related to each of the following?
 - the anesthetic effect of acupuncture
 - the absence of pain in a badly wounded soldier
 - the addiction of some people to long-distance running
- Are all drugs toxic? Explain your answer.

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chapter 24

Chemical Toxicology: Hemlock, Anyone?

When the Greek philosopher Socrates was accused of corrupting the youth of Athens in 399 B.C., he was given the choice of exile or death. He chose death and implemented his decision by drinking a cup of hemlock.

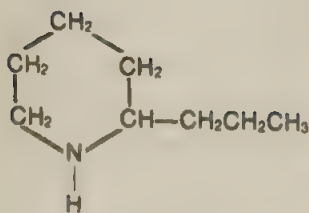
Poisons from plant and animal sources were well known in the ancient world. Snake and insect venoms were used, as were plant alkaloids. Today, many primitive tribes still know and use a variety of poisons in hunting and warfare. Curare (chapter 23), used by certain South American tribes, is one of the more notorious examples.

Although poisonous substances have been known and used for centuries, it is only within the last 150 years that scientists have learned the nature of the chemicals that are the active components of the various poisons. Socrates' hemlock probably was prepared from the fully grown but unripened fruit of *Conium maculatum* (poison hemlock). Usually, the fruit is dried carefully and then brewed into a "tea." Hemlock contains several alkaloids, but the principal one is coniine. This drug causes nausea, weakness, paralysis, and—as in the case of Socrates—death.

A study of the response of living organisms to drugs is called *pharmacology*. As we have seen (chapters 22 and 23), organisms respond in a variety of ways to the many chemical substances that we call drugs. In this chapter, we deal with those substances that are poisonous or otherwise injurious. *Toxicology* is the branch of pharmacology that deals with the effects of poisons, their identification or detection, and the development and use of antidotes.

All Things Are Poisons

What is a poison? Perhaps a better question would be "how much is a poison?" Substances may be harmless—or even necessary nutrients—in one amount and injurious—or even deadly—in another. Even common substances such as salt and sugar can be poisons when eaten in abnormally large amounts. Too much sugar—candy or other sweets—can give a child a stomachache. Too much salt—sodium



Coniine



Figure 24.1 Jacques Louis David's painting *The Death of Socrates* (1787) shows Socrates drinking the cup of hemlock to carry out the death sentence decreed by the rulers of Athens. (Courtesy of the Metropolitan Museum of Art, New York, Wolfe Fund, 1931.)

chloride—can act as an emetic. There have been cases of fatal poisoning when salt was accidentally substituted for lactose—milk sugar—in formulas for infants.

People also respond differently to the same chemical. To cite an extreme case, a few grams of sugar would cause no acute symptoms in a normal person but would be exceedingly dangerous to a diabetic. Excessive amounts of salt would be especially serious to a person with edema (swelling due to excessive amounts of fluid in the tissues).

Many drugs are also poisons (see **table 23.2** for some examples). In some cases, the effective dose of a drug is a significant fraction of the lethal dose. The usual dose of morphine is about 10 mg. As little as 70 mg can be fatal to some individuals. Other drugs, particularly some anticancer agents, are even more dangerous.

Pesticides can be poisonous to people as well as to pests. Some can be much more toxic to the intended pest species than to humans. Others, particularly pesticides aimed at other mammals (e.g., rodenticides), probably would be especially hazardous to people. A few poisons are species selective, but most are likely to be toxic to all—or nearly all—living cells.

Still another complicating factor is that chemicals behave differently when administered in different ways. Nicotine (**table 23.2**) is more than 50 times as toxic when applied intravenously as when taken orally. Good fresh water is delightful when taken orally, but even water can be deadly when inhaled in sufficient quantity. Further complications arise from the fact that even closely related animal species react differently to a given chemical. Even individuals within a species may react to different degrees.

In our discussion here, we cover only a few of the many toxic substances. These are organized into groups with similar activities. Those more likely to be encountered in everyday life are given priority.

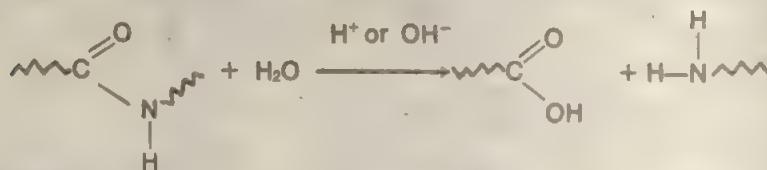
Corrosive Poisons: A Closer Look

In chapter 7, we examined the corrosive effect of strong acids and bases on human tissue. These chemicals indiscriminately destroy living cells. Corrosive chemicals, in lesser concentrations, also exert a more subtle effect.



Figure 24.2 *Conium maculatum* (poison hemlock).

Both acids and bases, even in dilute solutions, break down the protein molecules in living cells. These reactions involve the breaking of the amide (peptide) linkages in the molecules.



Protein molecule

Fragments

Since the reaction involves water, the process is called *hydrolysis*. Generally, the fragments are not able to carry out the functions of the original protein. In cases of severe exposure, the fragmentation continues until the tissue has been completely destroyed.

Acids in the lungs are particularly destructive. In chapter 19, we saw how sulfuric acid is formed when sulfur-containing coal is burned. Acids are formed also when plastics and other wastes are burned (chapter 14). The damage these pollutants do can be explained as the breakdown of lung tissue by the acids (chapter 19).

Other air pollutants also damage living cells. Ozone, peroxyacetyl nitrates (PAN), and the other oxidizing components of photochemical smog probably do their main damage through the deactivation of enzymes. The active sites of enzymes often incorporate the sulfur-containing amino acids cysteine and methionine. Cysteine is readily oxidized by ozone to cysteic acid.

Figure 24.3 The respiratory system, showing the route of air through the nose, pharynx (throat), larynx (voice box), and trachea (windpipe), into the bronchi and bronchioles (bronchial tubes) and ending in the alveoli (air sacs).

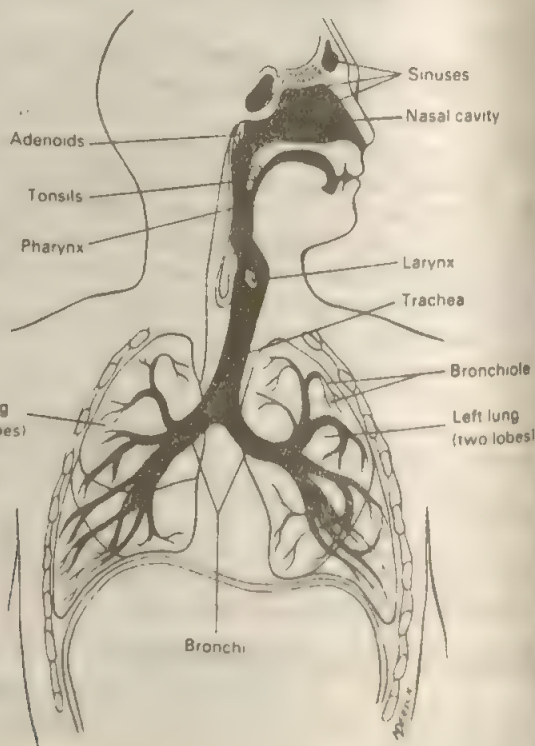
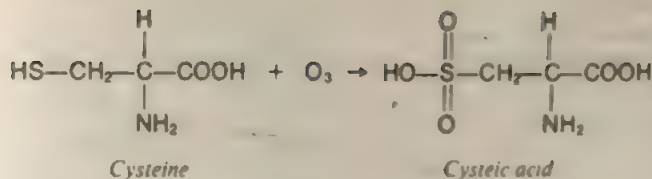
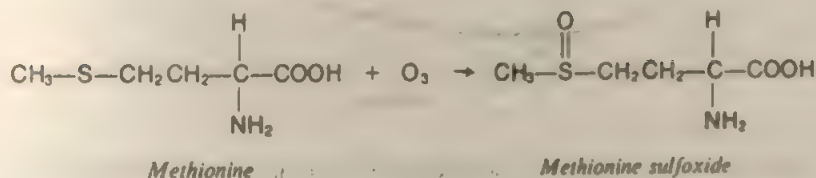


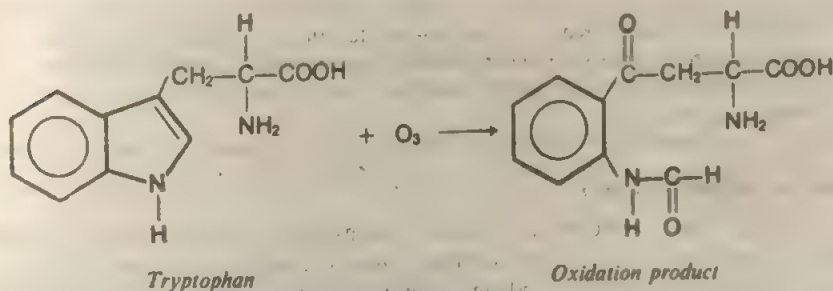
Figure 24.4 Pulmonary emphysema. The loss of elasticity and the deterioration of the alveoli walls deter the exhalation of carbon dioxide.



Methionine is oxidized to methionine sulfoxide.



Still another amino acid, tryptophan, is known to react with ozone. Tryptophan, which does not contain sulfur, undergoes a ring-opening oxidation.

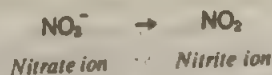


Most likely, oxidizing agents can break bonds in many of the chemical substances in a cell. Such powerful agents as ozone are more likely to make an indiscriminate attack than to react in a highly specific way.

Blood Agents

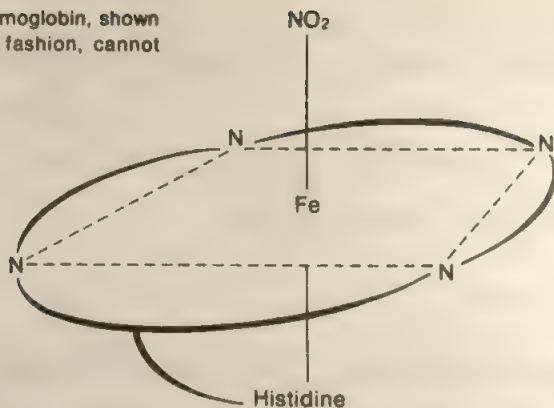
Certain chemical substances serve to block the transport of oxygen in the bloodstream or to prevent the oxidation of metabolites by oxygen in the cells. All act on the iron atoms in complex protein molecules. Probably the best known of these blood agents is carbon monoxide. The action of this lethal gas was described in chapter 19. Recall that carbon monoxide binds tightly to the iron atom in hemoglobin, blocking the transport of oxygen.

Nitrates, which occur in dangerous amounts in the groundwater in some agricultural areas (chapter 18), also serve to diminish the ability of hemoglobin to carry oxygen. Nitrates are reduced by microorganisms in the digestive tract to nitrites.



Nitrite ions may bond to the iron atoms in hemoglobin. The resulting nitrohemoglobin (figure 24.5) cannot carry oxygen. Its presence causes the victim to show signs of oxygen deficiency.

Figure 24.5 Nitrohemoglobin, shown here in schematic fashion, cannot carry oxygen.



The nitrate ion also may oxidize the iron atoms in hemoglobin from Fe^{2+} to Fe^{3+} . The resulting compound, called methemoglobin, is also incapable of carrying oxygen. The resulting oxygen-deficiency disease is called methemoglobinemia. In infants, this disease is called the blue baby syndrome.

Hemoglobin is bright red. It is responsible for the red color of the blood. Methemoglobin is brown. During the cooking process, red meat turns brown due to the oxidation of hemoglobin to methemoglobin. Dried blood stains turn brown for the same reason.

Cyanide: Agent of Death

Cyanide is one of the most notorious poisons in both fact and fiction. It acts almost instantaneously and only a minute amount constitutes a lethal dose. The average fatal dose is only 50 or 60 mg. Cyanide is used as gaseous hydrogen cyanide ($\text{H}-\text{C}\equiv\text{N}$) and as solid salts that contain the cyanide ion ($\text{C}\equiv\text{N}^-$). Hydrogen cyanide is used (with great care by specially trained experts) to exterminate insects and rodents in the holds of ships, in warehouses, in railway cars, and on citrus and other fruit trees. Sodium cyanide (NaCN) is used to extract gold and silver from their ores. It also is used in electroplating baths. Hydrogen cyanide is generated easily from the sodium salt by treatment with an acid.



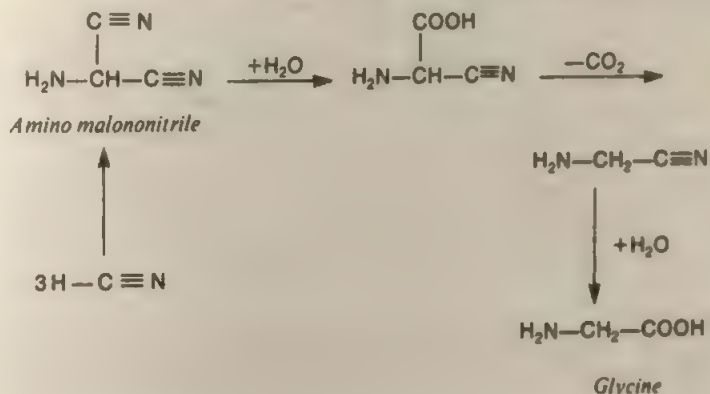
Unlike carbon monoxide, cyanide does not react with hemoglobin. Instead, it blocks the oxidation of glucose inside the cell by forming a stable complex with the oxidation enzymes. The enzymes, called cytochrome oxidases, contain iron and copper atoms. They normally act by providing electrons for the reduction of oxygen in the cell. Cyanide ties up those mobile electrons, rendering them unavailable for the reduction process. Thus, cyanide brings an abrupt end to cellular respiration, causing death in a matter of minutes.

Any antidote for cyanide poisoning must be administered quickly. The treatment of choice nowadays involves sodium thiosulfate (the "hypo" used in developing photographic film). The sulfur atom is transferred from the thiosulfate ion to the cyanide ion, converting the latter to relatively innocuous thiocyanate.

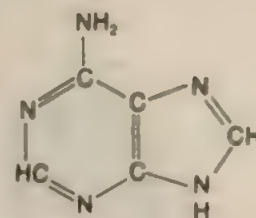
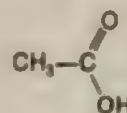


Unfortunately, few victims of cyanide poisoning survive long enough to be treated

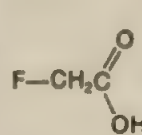
It is of interest to note that some researchers (reference 6) now speculate that life on Earth may have developed from molecules formed by the polymerization of hydrogen cyanide. This deadly gas is readily formed when an electric discharge is passed through a mixture of gases designed to simulate the Earth's early atmosphere. Many of the amino acids and the organic bases necessary to form DNA and RNA can be derived by the polymerization of HCN with the rearrangement of only a few atoms. Glycine, the simplest amino acid, can be derived from the trimer amino malononitrile by hydrolysis, decarboxylation, and a second hydrolysis.



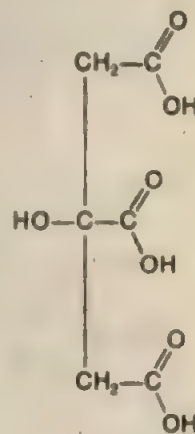
Simple inspection of the formula for adenine shows it to be a pentamer of HCN. Would it not indeed be ironic if life arose from compounds made from such a deadly poison?

Adenine
(HCN),

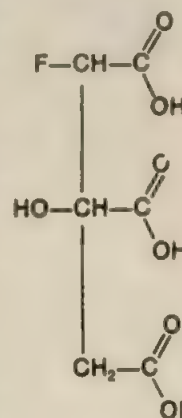
Acetic Acid



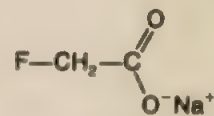
Fluoroacetic Acid



Citric Acid



Fluorocitric Acid



Sodium Fluoroacetate

Make Your Own Poison: Fluoroacetic Acid

Although the body generally acts to detoxify poisons (as we shall shortly see), there are notable exceptions in which the body converts an essentially harmless chemical into a deadly poison. Fluoroacetic acid is one such compound.

The body cells use acetic acid to produce citric acid. The citric acid is then broken down in a series of steps, most of which release energy. When fluoroacetic acid is ingested, it is incorporated into fluorocitric acid. The latter effectively blocks the citric acid cycle by tying up the enzyme which acts on citric acid. Thus the energy-producing mechanism of the cell is shut off and death rapidly ensues.

Sodium fluoroacetate (*Compound 1080*) is widely used to poison rats and predatory animals. It is not selective, and thus is highly dangerous to humans, pets, and other desirable animals. Sodium fluoroacetate was once widely used by ranchers to poison coyotes, eagles, and other animals suspected of preying on sheep and cattle. Such use drove the eagles nearly to extinction. As a result, poisoning of predators by use of sodium fluoroacetate and other deadly chemicals was banned on federal land.

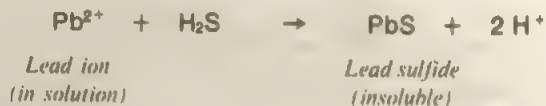
The Heavyweights: Metallic Poisons

People have long used a variety of metals in industry and agriculture and around the home. Most metals and their compounds show some toxicity when ingested in large amounts. Even the essential mineral nutrients (chapter 16) can be toxic when taken in excessive amounts. Quite often, too little of a metal (deficiency) can be as dangerous as too much (toxicity). For example, the average adult requires 10 to 18

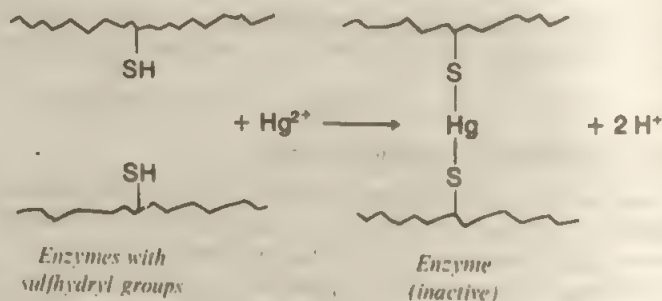
mg of iron each day. If less is taken in, the person suffers from anemia. Yet an overdose can cause vomiting, diarrhea, shock, coma, and even death. As few as 10 to 15 tablets containing 5 grains (324 mg) each of iron (as FeSO_4) have been fatal to children.

It is not known exactly how iron poisoning works. The heavy metals—those near the bottom of the periodic chart—exert their action primarily by inactivating enzymes.

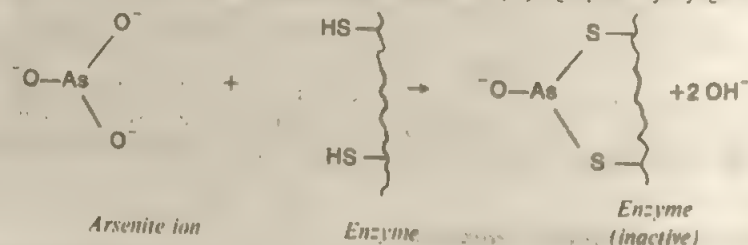
It is well known in inorganic chemistry that heavy metal ions react with hydrogen sulfide (H_2S) to form insoluble sulfides.



Most enzymes have amino acids with sulfhydryl ($-\text{SH}$) groups at or near the active sites. Heavy-metal ions tie up these groups, rendering the enzyme inactive.



The infamous poison arsenic is not a metal but has some metallic properties. In commercial poisons, arsenic usually is found as arsenate (AsO_4^{3-}) or arsenite (AsO_3^{3-}) ions. These also render enzymes inactive by tying up sulfhydryl groups.



Organic compounds containing arsenic are well known. One such compound, arsphenamine, was the first antibacterial. It once was used widely in the treatment of syphilis. Another arsenic compound was developed as a blister agent for use in chemical warfare. This agent was first synthesized by (and named for) W. Lee Lewis.

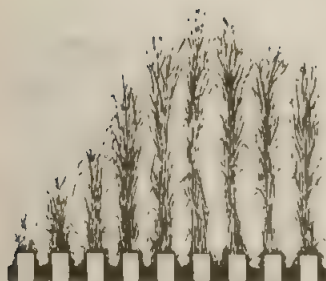
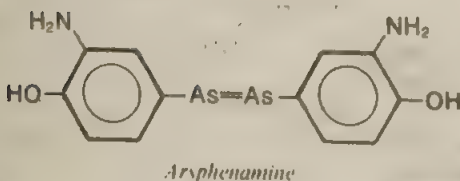
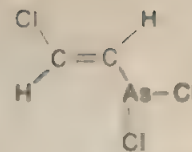


Figure 24.6 The effect of copper on the height of oat seedlings. From the left to the right, the quantities of copper present are 0, 3, 6, 10, 20, 100, 500, 2000, and 3000 μg per litre. (Redrawn from Piper, C. S., *Journal of Agricultural Science* 32:143 [1942].)

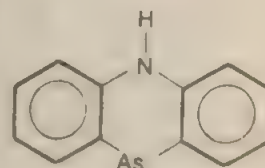


The United States started large-scale production of Lewisite in 1918. Lewisite is similar to mustard gas in its action, but its action is quicker and it incapacitates more readily. Fortunately, the war came to an end before this gas could be employed.

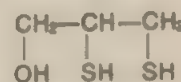
Still another arsenic-containing compound has found its way into our chemical arsenal. Called DM, this chemical is classified as a vomiting agent. It causes nausea and loosening of the bowels. The Department of Defense forbids its use in training exercises. Chemically, DM is diphenylamine chlorarsine. It was used in Vietnam as an incapacitating agent, although its use was not approved where casualties were not acceptable.



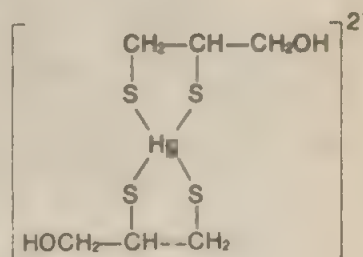
Lewisite



Agent DM



BAL



Mercury atom chelated by two BAL molecules

Quicksilver → Slow Death

Mercury (Hg) is a most unusual metal. It is the only common one that occurs as a liquid at room temperature. This bright, silvery, dense liquid—formerly known as quicksilver—has long held the fascination of people. Children sometimes play with the mercury from a broken thermometer, often with tragic results. Mercury vapor is hazardous. An open container or a few droplets spilled on the floor put enough mercury vapor into the air to exceed the established maximum safe level by a factor as large as 200.

Some of the problems of mercury in the environment were discussed in chapter 18. Mercury presents a greater hazard to those who work with it. Dentists use it to make amalgams for filling teeth. Laboratory workers use mercury and its compounds in a variety of ways. Farmers use seeds treated with compounds of mercury. Since mercury is a cumulative poison (it takes the body about 70 days to rid itself of half a given dose), chronic poisoning is a real threat to those continually exposed to it.

Fortunately, there are antidotes available for the treatment of mercury poisoning. British scientists, searching for an antidote for the arsenic-containing war gas Lewisite, came up with a compound effective for heavy-metal poisoning as well. The compound, a derivative of glycerol (chapter 16), came to be known as BAL (British Anti-Lewisite). BAL acts by chelating (Greek *chela*: "claw") the metal ion. Thus tied up, the mercury cannot attack the vital enzymes.

Now for the bad news. The symptoms of mercury poisoning may not show up for several weeks. By the time the symptoms—loss of equilibrium, sight, feeling, hearing—are recognizable, extensive damage has already been done to the brain and the nervous system. Such damage is largely irreversible. The BAL antidote is effective only when a person knows that he or she has been poisoned and seeks treatment right away.

Metallic mercury seems not to be very toxic when ingested (swallowed). Most of it passes through the system unchanged. Indeed, there are numerous reports of mercury being given orally as a remedy for obstruction of the bowels during the eighteenth and nineteenth centuries. Doses varied from a few ounces to a pound or more. Reports from the poison control center of the New York City Department of Health confirm the low toxicity of metallic mercury taken orally. Eighteen incidents without serious effects were noted over a 2-year period.

When inhaled, however, mercury vapor is quite hazardous, particularly when exposure occurs over a long period of time. Such chronic exposure usually involves mining, extraction, or regular occupational use of the metal. The body seems able to convert the inhaled mercury, by some as yet unknown mechanism, to Hg^{2+} ions. All the compounds of mercury, except those that are essentially insoluble in water, are poisonous no matter how they are administered.

Lead in the Environment

Compounds of the element lead (Pb) are widespread in the environment; this reflects the many uses that we have for this soft, dense, corrosion-resistant metal and for its compounds. Lead (as Pb^{2+}) is present in many foods, generally in concentrations of less than 0.3 ppm. However, condensed milk, sold in cans sealed with lead solder, may contain as much as 0.5 ppm (reference 27). Lead (again as Pb^{2+}) also gets into our drinking water (up to 0.1 ppm) from lead-sealed pipes. Lead compounds, mainly from automobiles that burn leaded gasoline, even permeate the air we breathe. (This exposure should decrease as we switch to unleaded gasoline.)

Lead compounds are quite toxic. Metallic lead is generally converted to Pb^{2+} in the body. So, with all that lead, why aren't we dead? The answer lies in the fact that we can excrete about 2 mg per day. Our intake from air, food, and water is generally less than that. If intake exceeds excretion, lead builds up in the body and chronic lead poisoning results.

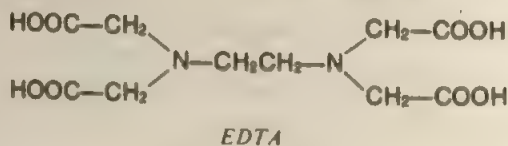
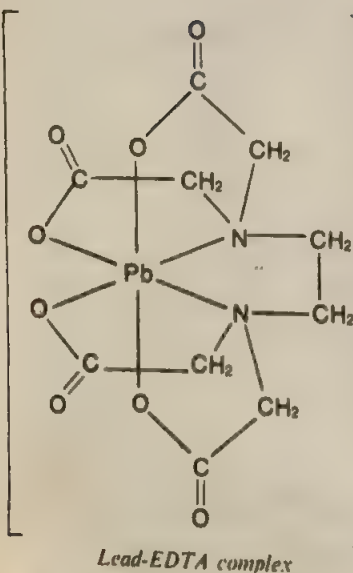
Lead poisoning is a major problem with children, particularly those in slum areas. Some children develop a craving that leads them to eat unusual things. This syndrome, called *pica*, causes them to eat chips of peeling, lead-based paints. These children probably also pick up lead compounds from the streets, where they are deposited by automobile exhausts. They also may get lead from metal toothpaste tubes, canned milk, and other sources. In all, 250 000 children suffer from lead poisoning each year. Such poisoning often leads to mental retardation and neurological disorders through damage to the brain and nervous system.

Lead poisoning usually is treated with a combination of BAL and another chelating agent called EDTA (ethylenediaminetetraacetic acid). The calcium salt of EDTA is administered intravenously. In the body, calcium ions are displaced by lead ions, which the chelate binds more tightly.



The lead-EDTA complex is excreted.

As with mercury poisoning, the neurological damage done by lead compounds is essentially irreversible. Treatment must be begun early in order to be effective.



Cadmium: The Ouch-Ouch Disease

Cadmium (Cd) is used less extensively than lead or mercury, but it too has caused major catastrophes. Cadmium is used widely in alloys, in the electronics industry, in nickel-cadmium rechargeable batteries, and many other applications. Cadmium poisoning leads to a loss of calcium ions (Ca^{2+}) from the bones, leaving them brittle and easily broken. It also causes severe abdominal pain, vomiting, diarrhea, and a choking sensation.

The most notable cases of cadmium poisoning occurred along the upper Zintsu River in Japan. The metal (as Cd^{2+}) entered the water in milling wastes from a mine. Downstream the water was used by farm families for drinking, cooking, and other household uses. It was also used to irrigate the rice fields. Soon the farm folk began to suffer from a strange, painful malady that became known as *itai-itai*, the "ouch-ouch" disease.

The Chemistry of the Nervous System

Some poisons—among them the most toxic substances known—act only upon the nervous system. In order to understand how these nerve poisons work, let's take a look at nerve cells and how they work. The nervous system is made up of about 10 billion nerve cells. These vary a great deal in shape and size. One type is shown in **figure 24.7**. The essential parts of each cell are the cell body, the axon, and the dendrites. We discuss here only those nerves that make up the involuntary (autonomic) nervous system. These nerves carry messages between the organs and glands that act involuntarily (such as the heart, the digestive organs, the lungs, etc.) and the brain and the spinal column.

Although the axons on a given nerve cell may be up to 60 cm long, there is no continuous pathway from an organ to the central nervous system. Messages must be transmitted across tiny fluid-filled gaps, or synapses (**figure 24.8**). When an electrical signal from the brain reaches the end of an axon, chemicals that carry the impulse across the synapse to the next cell are liberated. One such chemical is acetylcholine. It is thought to activate the next cell by changing the permeability of the cell membrane, perhaps allowing ions to flow through the membrane more readily.

Once acetylcholine has carried the impulse across the synapse, it is rapidly hydrolyzed to acetic acid and choline. This reaction is catalyzed by an enzyme, cholinesterase.

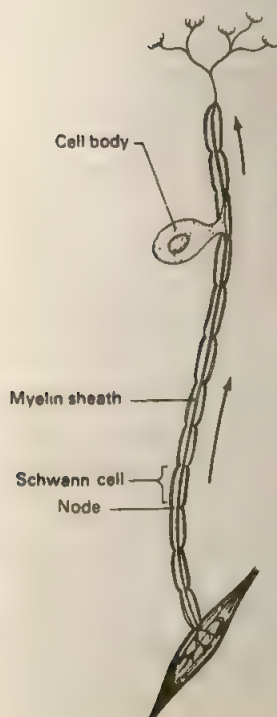
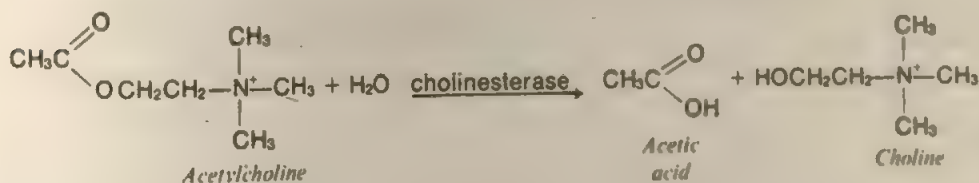


Figure 24.7 A human nerve cell. (Alter Keeton, William T., *Elements of Biological Science*, New York: W. W. Norton, 1967.)

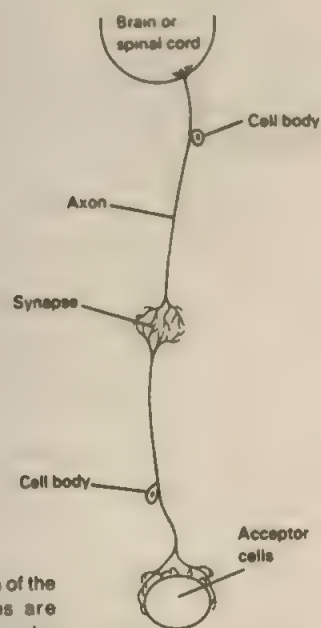


Figure 24.8 Schematic diagram of the pathway by which messages are transmitted to and from an acceptor cell in a gland or an organ to the central nervous system.

Choline is relatively inactive. This breakdown enables the receptor cell to receive further impulses. Other enzymes, such as acetylase, convert the acetic acid and choline back to acetylcholine, completing the cycle (figure 24.9).

Figure 24.9 The acetylcholine cycle.

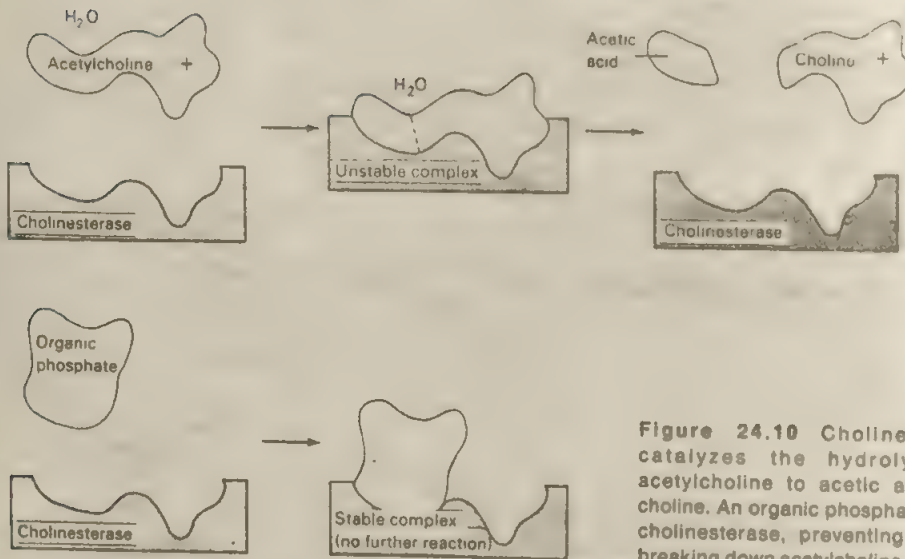
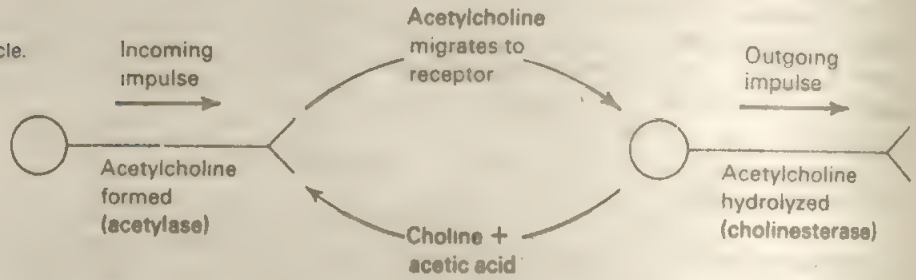


Figure 24.10 Cholinesterase catalyzes the hydrolysis of acetylcholine to acetic acid and choline. An organic phosphate ties to cholinesterase, preventing it from breaking down acetylcholine.

Nerve Poisons

Various chemical substances can disrupt the acetylcholine cycle at different points. Botulin, the deadly toxin given off by *Clostridium botulinum* (an anaerobic bacterium) in improperly processed canned food, blocks the synthesis of acetylcholine. With no messenger formed, no messages are carried. Paralysis sets in and death occurs, usually by respiratory failure.

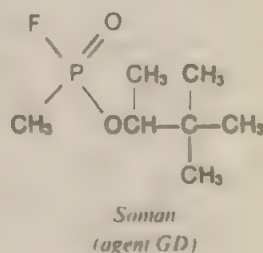
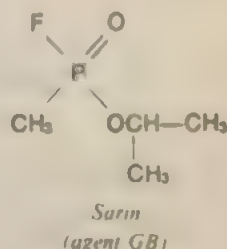
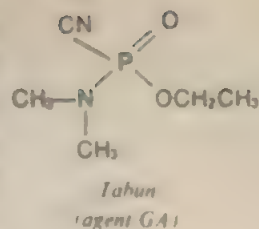
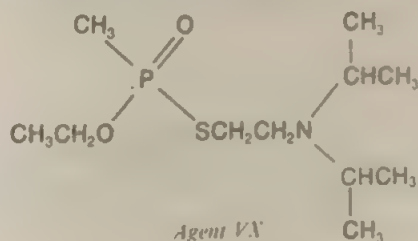
Curare, atropine, and some of the local anesthetics (chapter 23) act by blocking the receptor sites. In this case, the message is sent but not received. This can be good, in the case of local anesthetics, for relief from pain in a limited area. These drugs, too, can be fatal in sufficient quantity.

The third category of poisons, called anticholinesterase poisons, blocks the action of cholinesterase. The organic phosphorus insecticides (chapter 15) are well-known nerve poisons. The phosphorus-oxygen linkage is thought to bond tightly to cholinesterase. This blocks the breakdown of acetylcholine, and the acetylcholine builds up and causes the receptor nerves to fire repeatedly. This overstimulates the muscles, glands, and organs. The heart beats wildly and irregularly. The victim goes into convulsions and dies quickly.

While doing research on organic phosphates as possible insecticides during World War II, German scientists discovered some extremely toxic compounds with a frightening potential for use in warfare. The Russians captured a plant that manufactured a compound called Tabun (designated as agent GA by the United States Army). The Soviets dismantled the factory and moved it to Russia. The United States Army captured some of the stock, however. Presumably, the gas has been produced and stocked by both of the former allies.

The United States has developed other nerve poisons. One is called Sarin (agent GB). Sarin is four times as toxic as Tabun. It also has the "advantage" of being odorless. Tabun has a fruity odor. Another organophosphate nerve poison is Soman (agent GD). It is moderately persistent, whereas Tabun and Sarin are generally nonpersistent.

Still another nerve gas is the agent VX. Notice again the variation in structure from one compound to the next. The approach to developing chemical warfare agents is much the same as the approach for developing drugs—find one that works and then synthesize and test structural variations.



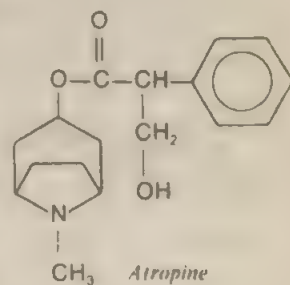
The nerve gases are among the most toxic synthetic chemicals known. They kill by inhalation or by absorption through the skin. They result in the complete loss of muscular coordination and subsequent death by cessation of breathing. The usual antidote is atropine injection and artificial respiration. Without the antidote, death may occur in 2 to 10 minutes.

The similarity of insecticides such as malathion and parathion to these nerve gases should be recognized. Though somewhat less toxic than the nerve gases, these phosphorus-based insecticides and others like them should be used with extreme caution.

Even the relatively safe (to mammals) chlorinated hydrocarbon pesticides act as nerve poisons. Acute DDT poisoning causes tremors, convulsions, and cardiac or respiratory failure. Chronic exposure to DDT leads to the degeneration of the central nervous system.

Other chlorinated compounds, such as the PCBs (chapter 14), act in a similar manner. The chlorinated phenol hexachlorophene, once widely used in germicidal cleaning solutions (*Phisohex*) and as an ingredient in deodorant soaps and other cosmetics, has been banned from over-the-counter preparations because it causes neurological disease when used in high concentrations. It is still available by prescription and for hospital use, however, because it is one of the few germicides effective against deadly staph infections.

Nerve poisons aren't all bad. Even the nerve gases, with their tremendous potential for death and destruction, are not nearly as toxic as the natural toxin botulin. None has yet been used against human populations in war. And, most important, these frightening compounds have helped us gain an understanding of the chemistry of the nervous system. It is that knowledge that enables scientists to design

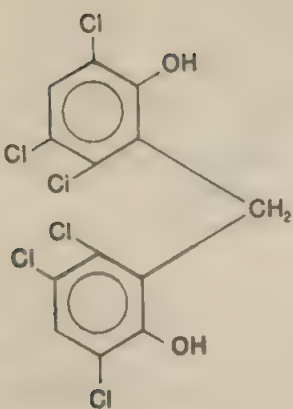


antidotes for the nerve poisons. In addition, our increased understanding should contribute to progress along more positive lines—in the control of pain, for example.

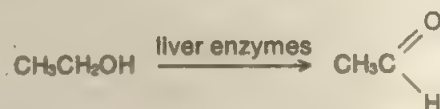
Your Liver: A Detox Tank

The human body is able to handle a moderate amount of some poisons. The liver is able to detoxify some compounds by oxidation, reduction, or coupling with amino acids or other normal body chemicals.

Perhaps the most common route is oxidation. Ethyl alcohol is detoxified by oxidation to acetaldehyde.

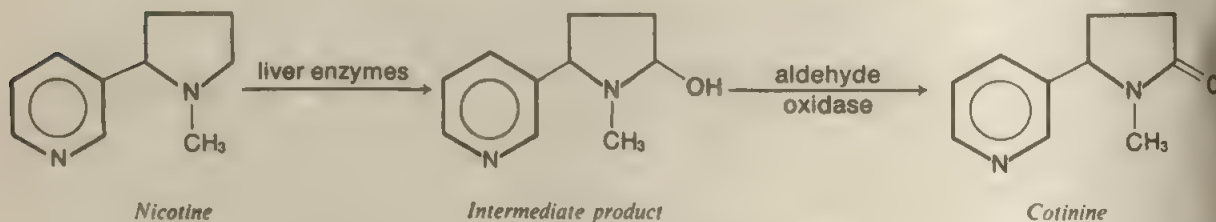


Hexachlorophene



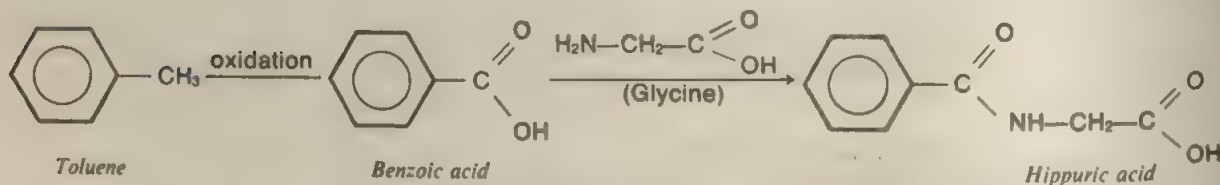
The acetaldehyde, in turn, is oxidized to acetic acid, a normal constituent of cells. The acetic acid then can be oxidized to carbon dioxide and water.

Highly toxic nicotine from tobacco smoke is detoxified by oxidation to cotinine.



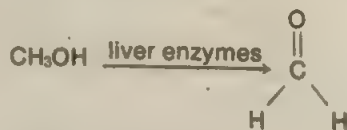
Cotinine has very little toxicity.

Toluene, an aromatic hydrocarbon, is detoxified in the liver by oxidation to benzoic acid, followed by conjugation with glycine.



The end product, hippuric acid (an inactive metabolite), is excreted.

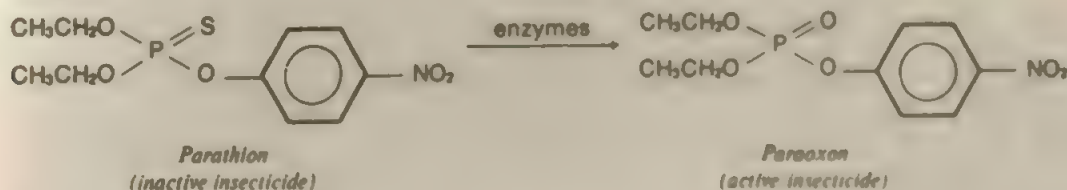
It should be pointed out that the liver enzymes just oxidize, reduce, or conjugate. The end product is not always less toxic. For example, methyl alcohol is oxidized to much more toxic formaldehyde.



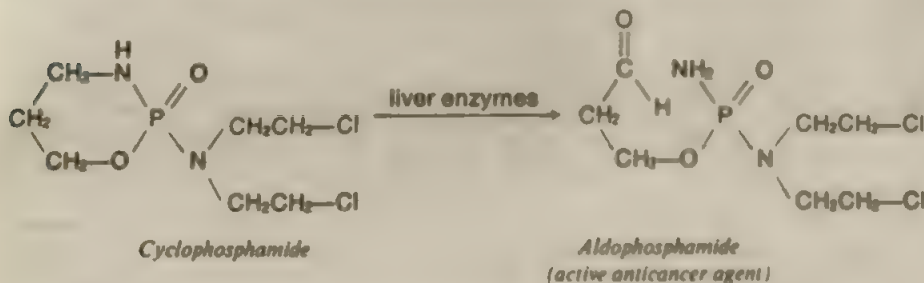
It is of interest to note that the same enzymes that oxidize the alcohols deactivate the male hormone testosterone. Buildup of these enzymes in a chronic alcoholic leads to a more rapid destruction of testosterone. Thus, we have the mechanism for alcoholic impotence, one of the well-known characteristics of the disease.

An antidote for methyl alcohol poisoning is ethyl alcohol. Ethyl alcohol is administered intravenously in an attempt to "load up" the liver enzymes with ethyl alcohol and thus to block the oxidation of methyl alcohol until it can be excreted.

Enzymes also serve to activate parathion. The sulfur-containing insecticide is itself inactive, but it is transformed biochemically into paraoxon, an agent resembling the nerve gases.



Some drugs also are activated in the liver. Cyclophosphamide, the anticancer drug (chapter 22), is converted to the active aldophosphamide by liver enzymes.



And, as we see shortly, some carcinogens are activated in the liver, as well.

Chemical Carcinogens: The Slow Poisons

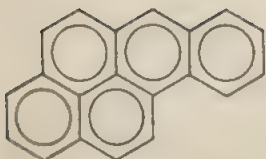
In earlier chapters, we mentioned carcinogens often. These substances cause the growth of *tumors*. A tumor is an abnormal growth of new tissue. It may be *benign*; benign tumors are characterized by their very slow growth. They often regress spontaneously, and they do not invade neighboring tissues. *Malignant* tumors often are called *cancers*. They may grow slowly or rapidly, but their growth is generally irreversible. Cancers invade and destroy neighboring tissues. Actually, cancer is not a single disease. It is a catchall term for over a hundred different afflictions. Many are not even closely related to each other.

What causes cancer? The World Health Organization estimates that 80% to 90% of the cases are caused by environmental factors and 10% to 20% by genetic factors and (perhaps) viruses. Included most prominently among those "environmental" causes are cigarette smoking (40%), dietary factors (25% to 30%), and occupational exposure (10%). That leaves 10% to 15% that may be caused by environmental

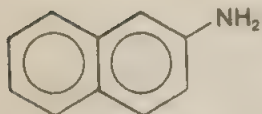
pollutants. In also should be noted that, contrary to popular opinion, "everything" does *not* cause cancer. Even among those chemicals that have been suspect, many cannot be shown to be carcinogenic. We are still left, though, with many compounds that are carcinogenic, and some of them are widely used.

Not all carcinogens are synthetic chemicals. Some, such as safrole in sassafras and the aflatoxins produced by molds on foods (chapter 17), occur naturally. Further, a variety of widely different chemical compounds are carcinogenic. We could not attempt to cover all the types of carcinogens here, but we concentrate on a few major classes.

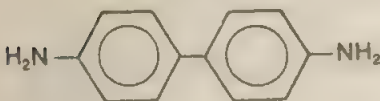
One of the more notorious types is the polycyclic aromatic hydrocarbons (chapter 10), of which 3,4-benzpyrene is perhaps the best known. Carcinogenic hydrocarbons are formed during the incomplete burning of nearly any organic material. They have been found in charcoal-grilled meats, cigarette smoke, automobile exhausts, coffee, burnt sugar, and many other materials. Not all polycyclic aromatic hydrocarbons are carcinogenic. There are strong correlations between certain molecular sizes and shapes and carcinogenicity. The mechanism of their action is currently under intense investigation. It already appears rather certain that the actual carcinogens are not the hydrocarbons themselves, but the oxidation products formed in the liver by the same enzymes that oxidize ethyl alcohol (p. 370).



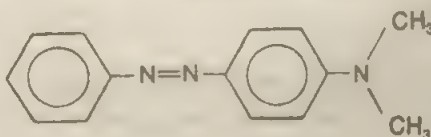
3,4-Benzpyrene



β -Naphthylamine



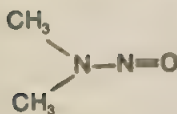
Benzidine



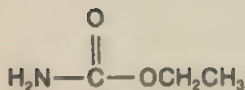
4-Dimethylaminoazobenzene



Vinyl chloride



Dimethylnitrosamine



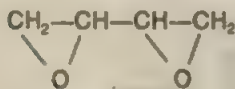
Ethyl carbamate

Another important class of carcinogens is the aromatic amines. Two prominent ones are β -naphthylamine and benzidine. These compounds once were used widely in the dye industry. They were responsible for a high incidence of bladder cancer among workers whose jobs brought them into prolonged contact with the compounds.

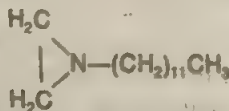
Several aminoazo dyes have been shown to be carcinogenic. An interesting example is 4-dimethylaminoazobenzene. This compound is also known as "butter yellow." It was used widely as a coloring for butter and oleomargarine before its carcinogenicity became known.

Not all carcinogens are aromatic. Prominent among the aliphatic (nonaromatic) ones are dimethylnitrosamine (chapter 17), vinyl chloride (chapter 14), and ethyl carbamate (chapter 23). Others include three- and four-membered heterocyclic rings containing nitrogen or oxygen. The epoxides and derivatives of ethyleneimine are examples. Others are cyclic esters called lactones.

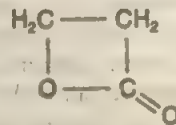
Keep in mind that this list is not all-inclusive. Rather, its purpose is to give you an idea of the kinds of compounds that have tumor-inducing properties, and the list grows almost daily as the results of ongoing research are released.



bis-Epoxybutane



N-Lauryl ethyleneimine



β -Propiolactone

How do chemicals cause cancer? Their mechanisms of action are probably as varied as their chemical structure. Some carcinogens chemically modify DNA, thus scrambling the code for replication and for the synthesis of proteins. For example, aflatoxin B is known to bind to guanine residues in DNA. Just how this initiates cancer, however, is not known for sure.

Testing for Carcinogens: Three Ways

How do we know that a chemical causes cancer? Obviously, we can't experiment on humans to see what happens. Indeed, there is no way to prove *absolutely* that a chemical does or does not cause cancer in humans. There are, however, three ways to gain evidence against a compound: animal tests, epidemiological studies, and bacterial screening for mutagenesis.

Chemicals suspected of being carcinogens usually are tested on animals. Tests using low dosages on millions of rats would cost too much, so tests usually are done by using large doses on 50 or so rats. An equal number of rats serve as controls. The control group is exposed to the same diet and environment as the experimental group, except that the control group does not get the suspected carcinogen. A higher incidence of cancer in the experimental animals than in the controls indicates that the compound is carcinogenic.

Animal tests are not conclusive. Humans usually are not exposed to comparable doses, there may be a threshold below which a compound is not carcinogenic. Further, human metabolism is different from the metabolisms of other animals. The carcinogen might be active in the rat but not in humans (or vice versa). Despite the shortcomings of this method, there is good correlation between the animal tests and the occurrence of human cancers.

The best evidence that a substance causes cancer in humans comes from epidemiological studies. A population that has a higher than normal rate for a particular kind of cancer is studied for common factors in their backgrounds. It was this sort of study, for example, that showed that cigarette smoking causes lung cancer, vinyl chloride causes a rare form of liver cancer, and asbestos causes cancer of the lining of the pleural cavity (the body cavity that contains the lungs). These studies require sophisticated mathematical analyses. There is always the chance that some other (unknown) factor is involved in the carcinogenesis.

The third way to gain evidence that a substance may be carcinogenic is by use of a screening test developed by Bruce N. Ames of the University of California, Berkeley. The Ames tests use a variant of the bacterium *Salmonella typhimurium* to test for *mutations* (changes in genes). The test is simple and relatively inexpensive. However, it is probably the least accurate of the three methods of identifying carcinogens. Some chemicals that are mutagens are not carcinogens. To date, though, 90% of the chemicals that fail the Ames test have been carcinogens, as well as mutagens. One shortcoming of the Ames test is that some chemicals, not carcinogenic themselves, are converted to carcinogens by metabolism. These might well pass the Ames test and still cause cancer. A modification of the test uses metabolites from urine or feces in the screening process to overcome the problem.

The Ames test is seldom used alone. If an economically important compound fails the Ames test, it is subjected to animal testing. Epidemiological studies also may be done. It is interesting to note that saccharin has been found guilty of being a carcinogen by all three methods.

Birth Defects: Teratogens

Another group of toxic chemicals is those that cause birth defects. These substances are called *teratogens*. Perhaps the most notable teratogen is the tran-

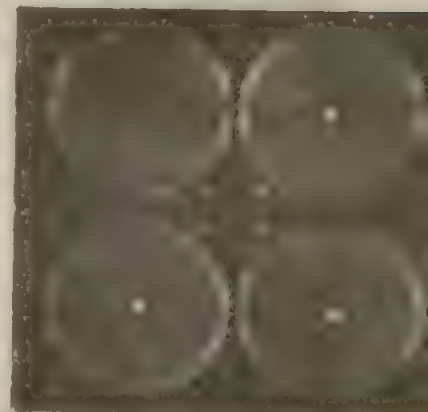
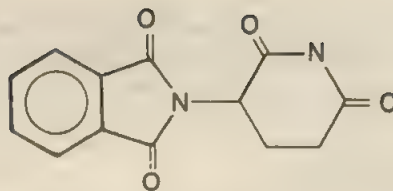


Figure 24.11 The spot test for mutagenic activity. Each petri plate contains, in a thin overlay of agar, the *Salmonella* test strain and, in plates C and D, a liver microsomal activation system. Mutagens are applied to filter-paper discs, which then are placed in the center of each plate. A holds spontaneous revertants; B, the Japanese food additive furylfuramide; C, the mold carcinogen aflatoxin B₁. Mutagen-induced revertants appear in a ring of colonies around each disc. (Reprinted with permission from Ames, B. N., McCann, J., and Yamasaki, E., *Mutagen Research* 31:347 [1975].)



Thalidomide

quilizer thalidomide. This drug was linked to a great tragedy during the late 1950s and early 1960s. Thalidomide was considered so safe, based on laboratory studies, that it often was prescribed for pregnant women and, in Germany, was available without a prescription. It took several years for the human population to provide evidence that laboratory animals had not. The drug had a disastrous effect on developing human embryos. Children born to women who had taken the drug during the first 12 weeks of pregnancy suffered from phocomelia, a condition characterized by shortened or absent arms and legs and other physical defects. The drug was used widely in Germany and Great Britain, and these two countries bore the brunt of the tragedy. The United States escaped relatively unscathed because an official of the Food and Drug Administration had believed there was evidence to doubt the drug's safety and had not, therefore, approved it for use in the United States.

There may be other chemicals that act as teratogens. More careful testing, however, has helped us to avoid another thalidomide tragedy. Indeed, some now say that our testing procedures are too strict, expensive, and time-consuming, and that they keep needed drugs off the market for years.

What Price Poisons?

We use so many poisons in and around our homes and work places that accidents are bound to happen. Poison-control centers have been established in several cities to help physicians deal with emergency poisonings. Are our insecticides, drugs, cleansers, and other chemicals worth the price we pay in terms of accidental poisonings? That is for you to decide really. Generally, it is the *misuse* of these chemicals that leads to tragedy.

Perhaps it is easy to be negative about chemists and chemistry when you think of such horrors as nerve gases, carcinogens, and teratogens. But keep in mind that many toxic chemicals are of enormous benefit to us and that they can be used safely despite their hazardous nature. The plastics industry was able to control vinyl chloride emissions once the hazard was known. We still are able to have valuable vinyl plastics, even though the vinyl chloride from which they are made causes cancer.

Increasingly, we will find ourselves having to decide whether the benefits we gain from a chemical substance outweigh the risks we assume by using it. I hope that the chemistry you have learned in this course will help you to make intelligent decisions. I hope most of all, though, that you will continue to learn chemistry throughout the rest of your life, for chemistry affects nearly everything that you do. I wish you success and happiness in your chosen profession. I hope that your knowledge of chemistry enriches your life. May the joy of learning go with you always.

Problems

1. How do dilute solutions of acids and bases damage living cells?
2. How does ozone damage living cells?



Figure 24.12 Dr. Frances Kelsey, of the United States Food and Drug Administration, discovered that the tranquilizing drug thalidomide caused gross deformities in babies. This discovery in applied research prevented the use of this drug for morning sickness and saved many a mother from the tragedy of giving birth to a "thalidomide baby." (Courtesy of the United States Food and Drug Administration, Washington, D.C.)

3. How does fluorouacetic acid exert its toxic effect?
4. Describe three ways in which the acetylcholine cycle can be stopped. Give examples of poisons that work each way.
5. Should toxic substances be tested on laboratory animals?
6. How does BAL work as an antidote for mercury poisoning?
7. How does EDTA work as an antidote for lead poisoning?
8. How does atropine work as an antidote for poisoning by an organic phosphate? (Hint: See p. 368.)
9. How does ethyl alcohol work as an antidote for methyl alcohol poisoning?
10. Do liver enzymes always detoxify foreign substances?
11. How can one poison serve as an antidote for another poison?
12. Are nerve gases less humane than bullets in warfare?
13. What are blood agents? How do they work?
14. How does cyanide exert its toxic effect?
15. How does thiosulfate act as an antidote for cyanide poisoning?
16. How do mercury and lead exert their toxic effects?
17. What is a carcinogen? A mutagen? A teratogen?
18. Give an example of each of the following types of carcinogens.
 - a. a polycyclic aromatic hydrocarbon
 - b. an aromatic amine
 - c. an aminoazo dye
 - d. a simple aliphatic compound
19. What are the three ways to test a compound for carcinogenicity? What are the limitations of each method?

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appendix A

The International System of Measurement

Metric measurement was discussed in some detail in chapter 1. Further discussion and additional tables are provided here.

The standard unit of length in the International System of Measurement is the *metre*. This distance was once meant to be 0.000 000 1 of the Earth's quadrant, that is, of the distance from the North Pole to the equator measured along a meridian. The quadrant was difficult to measure accurately. Consequently, for many years the metre was defined as the distance between two etched lines on a metal bar (made of a platinum-iridium alloy) kept in the International Bureau of Weights and Measures at Sèvres, France. Today, the metre is defined even more precisely as being 1 650 763.73 times the wavelength of the orange-red line in the spectrum of krypton-86.

The primary unit of mass is the *kilogram* (1 kg = 1000 g). It is based on a standard platinum-iridium bar kept at the International Bureau of Weights and Measures. The *gram* is a more convenient unit for many chemical operations.

The basic SI unit of volume is the cubic metre. The unit more frequently employed in chemistry, however, is the *litre* (1 L = 0.001 m³). All other SI units of length, mass, and volume are derived from these basic units.

Table A-1
Some SI prefixes and their relationship to the basic units

Prefix	Connotation
Pico-	0.000 000 000 001 × (or 10 ⁻¹² ×)
Nano-	0.000 000 001 × (or 10 ⁻⁹ ×)
Micro-	0.000 001 × (or 10 ⁻⁶ ×)
Milli-	0.001 × (or 10 ⁻³ ×)
Centi-	0.01 × (or 10 ⁻² ×)
Deci-	0.1 × (or 10 ⁻¹ ×)
Deka-	10 × (or 10 ¹ ×)
Hecto-	100 × (or 10 ² ×)
Kilo-	1 000 × (or 10 ³ ×)
Mega-	1 000 000 × (or 10 ⁶ ×)
Giga-	1 000 000 000 × (or 10 ⁹ ×)
Tera-	1 000 000 000 000 × (or 10 ¹² ×)

Table A-2
Some metric units of length

1 kilometre (km)	= 1000 metres (m)
1 metre (m)	= 100 centimetres (cm)
1 centimetre (cm)	= 10 millimetres (mm)
1 millimetre (mm)	= 1000 micrometres (μm)

Table A-3
Some metric units of mass

1 kilogram (kg)	= 1000 grams (g)
1 gram (g)	= 1000 milligrams (mg)
1 milligram (mg)	= 1000 micrograms (μg)

Table A-4
Some metric units of volume

1 litre (L)	= 1000 millilitres (mL)
1 millilitre (mL)	= 1000 microlitres (μL)
1 millilitre (mL)	= 1 cubic centimetre (cm ³)

Table A-5
Some English-metric conversions

<i>Length</i>	
1 mile (mi) = 1.61 kilometres (km)	
1 yard (yd) = 0.914 metre (m)	
1 inch (in) = 2.54 centimetres (cm)	
<i>Mass</i>	
1 pound (lb) = 454 grams (g)	
1 ounce (oz) = 28.4 grams (g)	
1 pound (lb) = 0.454 kilogram (kg)	
1 grain (gr) = 0.0648 gram (g)	
1 carat (car) = 200 milligrams (mg)	
<i>Volume</i>	
1 U.S. quart (qt) = 0.946 litre (L)	
1 U.S. pint (pt) = 0.473 litre (L)	
1 fluid ounce (fl oz) = 29.6 millilitres (mL)	
1 gallon (gal) = 3.78 litres (L)	

Table A-6
Some conversion units for pressure

1 millimetre of mercury (mm Hg) = 1 torr
1 atmosphere (atm) = 760 millimetres of mercury (mm Hg) = 760 torrs
1 atmosphere (atm) = 29.92 inches of mercury (in. Hg) = 14.7 pounds per square inch (psi)

Table A-7
Some temperature equivalents *

<i>Phenomenon</i>	<i>Fahrenheit</i>	<i>Celsius</i>
Absolute zero	-459.69 °F	-273.16 °C
Nitrogen boils/liquifies	-320.4 °F	-195.8 °C
Carbon dioxide solidifies/sublimes	-109.3 °F	-78.5 °C
Bitter cold night, northern Minnesota	-40 °F	-40 °C
Cold night, Indiana	0 °F	-18 °C
Water freezes/ice melts	32 °F	0 °C
Pleasant room temperature	72 °F	22 °C
Body temperature	98.6 °F	37.0 °C
Very hot day	100 °F	38 °C
Water boils/steam condenses	212 °F	100 °C
Temperature for baking biscuits	450 °F	232 °C

*Keep these equations in mind.

$$^{\circ}\text{F} = \frac{9}{5} (^{\circ}\text{C}) + 32$$

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32) \frac{5}{9}$$

Table A-8
Some conversion units for energy

1 calorie (cal) = 4.184 joules (J)
1 British thermal unit (Btu) = 1053 joules (J) = 252 calories (cal)
1 food Calorie = 1 kilocalorie (kcal) = 1000 calories (cal) = 4184 joules (J)

appendix B

Exponential Notation

Scientists often use numbers that are so large—or so small—that they boggle the mind. For example, light travels at 30 000 000 000 cm/second. There are 602 300 000 000 000 000 000 000 carbon atoms in 12 g of carbon. On the small side, the diameter of an atom is about 0.000 000 000 1 m. The diameter of an atomic nucleus about 0.000 000 000 001 m.

It is obviously difficult to keep track of the zeros in such quantities. Scientists find it convenient to express such numbers as powers of ten. Tables B-1 and B-2 contain partial lists of such numbers.

The speed of light is usually expressed as 3×10^{10} (i.e., $3 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10$) cm/second. The mass of an atom of cesium (Cs) is expressed as 2.21×10^{-23} g, that is, as

2.21 x 1 / 10 000 000 000 000 000 000 000

Numbers such as 10^6 are called exponential numbers, where 10 is the base and 6 is the exponent. Numbers in the form 6.02×10^{23} are said to be written in scientific notation.

Table B-1
Positive powers of ten

$10^0 = 1$
$10^1 = 10$
$10^2 = 10 \times 10 = 100$
$10^3 = 10 \times 10 \times 10 = 1000$
$10^4 = 10 \times 10 \times 10 \times 10 = 10\,000$
$10^5 = 10 \times 10 \times 10 \times 10 \times 10 = 100\,000$
$10^6 = 10 \times 10 \times 10 \times 10 \times 10 \times 10 = 1\,000\,000$
$10^{13} = 100\,000\,000\,000\,000\,000\,000\,000$

Table B-2
Negative powers of ten

$10^{-1} = 1/10 = 0.1$
$10^{-2} = 1/100 = 0.01$
$10^{-3} = 1/1\,000 = 0.001$
$10^{-4} = 1/10\,000 = 0.0001$
$10^{-5} = 1/100\,000 = 0.00001$
$10^{-6} = 1/1\,000\,000 = 0.000001$
$10^{-13} = 1/10\,000\,000\,000\,000\,000\,000\,000 = 0.000\,000\,000\,000\,1$

Exponential numbers are often used in calculations. The most common operations are multiplication and division. Two rules must be followed: (1)

to multiply exponentials, add the exponents, and (2) to divide exponentials, subtract the exponents. These rules can be stated algebraically as

(x^a) (x^b) = x^{a+b}

x^a / x^b = x^{a-b}

Some examples follow

(10^4)(10^4) = 10^{4+4} = 10^8

(10^4)(10^{-4}) = 10^{4+(-4)} = 10^{4-4} = 10^0

(10^{-5})(10^2) = 10^{-5+2} = 10^{-5-2} = 10^{-7}

(10^{-7})(10^{-3}) = 10^{-7+(-3)} = 10^{-7-3} = 10^{-10}

10^{14} / 10^4 = 10^{14-4} = 10^{10}

10^6 / 10^{23} = 10^{6-23} = 10^{-17}

10^{-10} / 10^{-6} = 10^{-10-(-6)} = 10^{-10+6} = 10^{-4}

10^3 / 10^{-2} = 10^{3-(-2)} = 10^{3+2} = 10^5

10^{-8} / 10^4 = 10^{-8-4} = 10^{-12}

10^7 / 10^7 = 10^{7-7} = 10^0 = 1

Problems involving both a coefficient (a numerical part) and an exponential are solved by multiplying (or dividing) coefficients and exponentials separately.

Example B-1 To what is the following expression equivalent?

(1.2 x 10^3) (2.0 x 10^4)

First, multiply the coefficients.

1.2 x 2.0 = 2.4

Then multiply the exponentials

10^3 x 10^4 = 10^{3+4} = 10^7

The complete answer is

2.4 x 10^7

Example B-2 To what is the following expression equivalent?

$$\frac{(8.0 \times 10^{11})}{(1.6 \times 10^4)}$$

First, divide the coefficients.

$$\frac{8.0}{1.6} = 5.0$$

Then divide the exponentials.

$$\frac{10^{11}}{10^4} = 10^{11-4} = 10^7$$

The answer is

$$5.0 \times 10^7$$

Example B-3 Give an equivalent for the following expression.

$$\frac{(1.2 \times 10^{14})}{(4.0 \times 10^6)}$$

It is convenient, before carrying out the division, to rewrite the dividend (the numerator) so that the coefficient is larger than that of the divisor (the denominator).

$$1.2 \times 10^{14} = 12 \times 10^{13}$$

Note that the coefficient was made larger by a factor of 10 and the exponential was made smaller by a factor of 10. The quantity as a whole is unchanged. Now divide.

$$\frac{12 \times 10^{13}}{4.0 \times 10^6} = 3.0 \times 10^7$$

Example B-4 Give an equivalent for the following expression.

$$\frac{(3 \times 10^7)(8 \times 10^{-2})}{(6 \times 10^3)(2 \times 10^{-1})}$$

In problems such as this, you can carry out the multiplications specified in the numerator and in the denominator separately and then divide the resulting numbers.

$$(3 \times 10^7)(8 \times 10^{-2}) = 24 \times 10^5$$

$$(6 \times 10^3)(2 \times 10^{-1}) = 12 \times 10^2$$

$$\frac{24 \times 10^5}{12 \times 10^2} = 2 \times 10^3$$

The multiplications and divisions in problems like this can be carried out in any convenient order.

There is only one other mathematical function involving exponentials that is of importance to us. What happens when you raise an exponential to a power? You just multiply the exponent by the power. To illustrate:

$$(10^3)^3 = 10^9$$

$$(10^{-2})^4 = 10^{-8}$$

$$(10^{-5})^{-3} = 10^{15}$$

If the exponential is combined with a coefficient, the two parts of the number are dealt with separately, as in the following example.

$$(2 \times 10^3)^2 = 2^2 \times (10^3)^2 = 4 \times 10^6$$

For a further discussion of—and more practice with—exponential numbers, see one of the following references.

1. Goldish, Dorothy M., *Basic Mathematics for Beginning Chemistry*, 2nd ed., New York: Macmillan, 1979. Chapter 3 covers exponential notation.
2. Loebel, Arnold B., *Chemical Problem Solving by Dimensional Analysis*, 2nd ed., Boston: Houghton Mifflin, 1978. Chapter 1, section A, deals with exponential notation.

appendix C

Solving Problems by Dimensional Analysis

A helpful method for solving problems like those encountered in this text is an approach called *dimensional analysis* or, sometimes, the *unit-factor method* or the *factor-label method*. The method employs the dimensions, or units, associated with a quantity as an aid in setting up the problem.

Quantities can be expressed in a variety of units. For example, you can buy beverages by the 12-oz can or by the pint, quart, gallon, or litre. If you wish to compare prices, you must be able to *convert* from one unit to another. To do this, one multiplies the original quantity by a *conversion factor*. Such a conversion changes the numbers and units involved but does not change the quantity. Your height, for example, is the same whether it is expressed in inches, feet, centimetres, or metres.

You know that multiplying a number by 1 doesn't change its value. Multiplying by a fraction equal to 1 also leaves the value unchanged. A fraction is equal to 1 when the numerator is equal to the denominator. For example, we know that

$$1 \text{ ft} = 12 \text{ in.}$$

Therefore, the fraction

$$\frac{1 \text{ ft}}{12 \text{ in.}} = 1$$

Similarly

$$\frac{12 \text{ in.}}{1 \text{ ft}} = 1$$

If we wish to convert from inches to feet we can do so by choosing one of the fractions as a conversion factor. *Which* one do we choose? The one that gives us an answer with the right units! Let's illustrate by an example.

Example C-1 My bed is 72 in. long. What is its length in feet?

Ignoring the smart alecks who immediately shouted out the answer, we shall proceed to show *how* the solution is obtained using the appropriate conversion factor. We need to multiply 72 in. by one of the above fractions. Which one? Let's try the first.

$$72 \text{ in.} \times \frac{1 \text{ ft}}{12 \text{ in.}} = 6 \text{ ft}$$

Note that the unit *inches* cancels, leaving us with an answer of 6 ft.

Reasonable. A bed might well be 6 ft long. Just for kicks, though, let's try the other conversion factor.

$$72 \text{ in.} \times \frac{12 \text{ in.}}{1 \text{ ft}} = 864 \text{ in.}^2/\text{ft}$$

Absurd! How can a bed be 864 in.²/ft?

You should have no difficulty choosing between the two possible

EXAMPLE

Example C-2 A recipe calls for 74 mL of milk. You have a measuring cup that measures in fluid ounces. How many ounces of milk would you need (1 fl oz = 29.6 mL)?

$$74 \text{ mL} \times \frac{1 \text{ fl oz}}{29.6 \text{ mL}} = 2.5 \text{ fl oz}$$

Notice that the unit millilitres must appear in the *denominator* of the conversion factor. (If you're not convinced, try it the other way.)

Example C-3 How many cubic centimetres of a penicillin preparation should be administered to a patient if the doctor's prescription specifies a dose of 600 000 units and the label on the penicillin container states that there are 150 000 units per cubic centimetre?

The 600 000 units must be converted to a value in cubic centimetres. The label gives the conversion factor (150 000 units = 1 cc).

$$600\,000 \text{ units} \times \frac{1 \text{ cc}}{150\,000 \text{ units}} = 4 \text{ cc}$$

Example C-4 The SI unit of energy is the joule. If your doctor puts you on a diet of 6 MJ per day, how many food Calories (kilocalories) is that? (1 food Calorie = 4184 joules and 1 MJ = 1 000 000 J).

$$6 \text{ MJ} \times \frac{1\,000\,000 \text{ J}}{1 \text{ MJ}} \times \frac{1 \text{ food Calorie}}{4184 \text{ J}} = 1434 \text{ food Calories}$$

It is possible (and frequently necessary) to manipulate units in the denominator as well as the numerator of a problem. Just remember to use conversion factors in such a way that the unwanted units cancel.

Example C-5 At a track meet a runner completes the mile in 4 minutes. How fast is this in miles per hour?

$$\frac{1 \text{ mi}}{4 \text{ minutes}} \times \frac{60 \text{ minutes}}{1 \text{ hour}} = 15 \text{ mi/hour}$$

Example C-6 A sprinter runs the 100-yd dash in 10 seconds. How fast is this in miles per hour?

This problem calls for the manipulation of units in both the numerator and the denominator.

$$\frac{100 \text{ yd}}{10 \text{ seconds}} = x \text{ mi/hour}$$

Let us assume that we have no direct conversion factors between yards and miles or between seconds and hours. We'll set up the problem with the following factors.

$$3 \text{ ft} = 1 \text{ yd}$$

$$5280 \text{ ft} = 1 \text{ mi}$$

$$1 \text{ minute} = 60 \text{ seconds}$$

$$1 \text{ hour} = 60 \text{ minutes}$$

First, let's set up the factors which will convert yards to miles.

$$\frac{100 \text{ yd}}{10 \text{ seconds}} \times \frac{3 \text{ ft}}{1 \text{ yd}} \times \frac{1 \text{ mi}}{5280 \text{ ft}} = x \text{ mi/second}$$

Next, let's incorporate the factors which will convert seconds to hours.

$$\frac{100 \text{ yd}}{10 \text{ seconds}} \times \frac{3 \text{ ft}}{1 \text{ yd}} \times \frac{1 \text{ mi}}{5280 \text{ ft}} \times \frac{60 \text{ seconds}}{1 \text{ minute}} \times \frac{60 \text{ minutes}}{1 \text{ hour}} = x \text{ mi/hour}$$

After carrying out all the indicated arithmetic we get the answer—20.5 mi/hour.

Here's one last problem just for fun.

Example C-7 If your heart beats 72 times per minute and your lifetime will be 70 years, how many times will your heart beat during your lifetime?

$$\frac{72 \text{ beats}}{1 \text{ minute}} \times \frac{60 \text{ minutes}}{1 \text{ hour}} \times \frac{24 \text{ hours}}{1 \text{ day}} \times \frac{365 \text{ days}}{1 \text{ year}} \times \frac{70 \text{ years}}{1 \text{ lifetime}} = 2\,650\,000\,000 \text{ beats/lifetime}$$

That's approaching 3 billion beats! Not bad for a bit of muscle the size of your fist!

For a more detailed discussion of this method of problem solving, consult one or more of the following sources.

1. Goldish, Dorothy M., *Basic Mathematics for Beginning Chemists*, 2nd ed., New York: Macmillan, 1979. Chapter 7 covers exponential notation.
2. Loebel, Arnold B., *Chemical Problem Solving by Dimensional Analysis*, 2nd ed., Boston: Houghton Mifflin, 1978.
3. Zahorowski, Leon M., and Hill, John W., *Chemical Problems for Changing Times*, Minneapolis: Burgess, 1973.

appendix D

Answers to Selected Problems

Chapter 1

- | | |
|----------------|-------------|
| 15. a. 1500 mm | d. 25.4 mm |
| b. 160 mm | e. 304.8 mm |
| c. 0.849 mm | |
| 16. a. 2.056 L | c. 0.54 L |
| b. 47 000 L | d. 4.7 L |
| 17. 690 kJ | |
| 18. a. 15 g | d. 0.047 L |
| b. 86 mg | e. 1364 mL |
| c. 149 mL | f. 19.8 qt |

Chapter 2

- | | |
|---|----------|
| 4. 11 g | |
| 9. 40 g H ₂ ; 9000 kg H ₂ O | |
| 10. a. 60 g | b. 600 g |
| 11. 4 | |

Chapter 3

- | | | |
|---|------------------|------------------|
| 5. a. 6e, 6p, 6n | c. 13e, 13p, 14n | e. 18e, 18p, 22n |
| b. 9e, 9p, 10n | d. 19e, 19p, 20n | f. 16e, 16p, 16n |
| 6. a. Li 2 1 | c. Si 2 8 4 | e. Ca 2 8 8 2 |
| b. N 2 5 | d. Cl 2 8 7 | f. P 2 8 5 |
| 7. 18; 32 | | d. 3 |
| 10. a. 4 | b. 8 | c. 7 |
| 11. metals: Fe, Na, Mg; nonmetals: C, Cl | | |
| 12. same group: Mg, Ca, Sr; same period: Mg, Al, Cl | | |

Chapter 4

3. $^{215}_{85}\text{At}$ (astatine-215)

4. a. 82p, 125n
b. 1p, 2n

c. 27p, 33n
d. 90p, 143n

5. $^{24}_{11}\text{Na}$ (sodium-24)

7. 1500; 750; 375

8. $^{235}_{92}\text{U}$ (uranium-235)

9. $^{239}_{92}\text{U} \rightarrow ^0_{-1}\text{e} + ^{239}_{93}\text{Np}$

11. 5730 years old; 11 460 years old

12. 24.6 years old

Chapter 5

1. a. $\text{Na}\cdot$

b. $\cdot\ddot{\text{F}}:$

c. $\cdot\ddot{\text{C}}:$

2. a. $\text{Na}^+:\ddot{\text{F}}:$

b. $\text{K}^+ \text{Cl}^-$

c. $\text{Mg}^{2+} 2:\ddot{\text{F}}:$

d. $\cdot\text{Mg}\cdot$

e. $\cdot\ddot{\text{N}}:$

f. $\cdot\ddot{\text{O}}:$

d. $2 \text{Na}^+:\ddot{\text{O}}:^-$

e. $3 \text{Na}^+ \text{N}^{3-}$

f. $\text{Mg}^{2+}:\ddot{\text{O}}:^-$

g. $\cdot\dot{\text{Al}}\cdot$

h. $\text{K}\cdot$

i. $\cdot\ddot{\text{Cl}}:$

g. $\text{Al}^{3+}:\ddot{\text{N}}:^-$

h. $\text{Al}^{3+} 3:\ddot{\text{Cl}}:$

i. $3 \text{Mg}^{2+} 2:\ddot{\text{N}}:^-$

6. ionic: KF, CaO, MgS, NaBr; nonpolar covalent: Br_2 , F_2 ; polar covalent: NO, IBr, HCl

7. a. H_2S , bent

b. SiH_4 , tetrahedral

c. BeCl_2 , linear

d. BF_3 , planar

8. a. X, group VII; Y, group VI; Z, Group V

b. $\text{H}:\ddot{\text{X}}:$

c. $:\ddot{\text{X}}:^-$

d. $\begin{array}{c} \ddot{\text{X}}:\ddot{\text{Y}}: \\ :\ddot{\text{X}}: \end{array}$

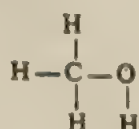
$\begin{array}{c} \text{H}:\ddot{\text{Y}}: \\ \text{H} \end{array}$

$:\ddot{\text{Y}}:^-$

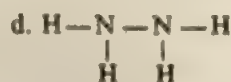
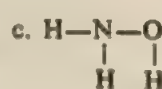
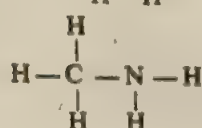
$\begin{array}{c} \ddot{\text{X}}:\ddot{\text{Z}}:\ddot{\text{X}}: \\ :\ddot{\text{X}}: \end{array}$

$\begin{array}{c} :\ddot{\text{Z}}:\text{H} \\ \text{H} \end{array}$

9. a.



b.



Chapter 6

1. a. C
b. Ca
c. Cl
d. Mg
2. a. hydrogen
b. nitrogen
c. oxygen
d. iron
3. a. NaBr
b. KI
c. CaO
d. AlCl₃
4. a. sodium bromide
b. calcium chloride
c. aluminum iodide
d. potassium oxide
e. sodium sulfide
5. a. NH₄Cl
b. NaCN
c. KNO₃
6. a. calcium sulfate
b. potassium carbonate
c. potassium bicarbonate (or potassium hydrogen carbonate)
d. sodium acetate
e. ammonium nitrite
f. potassium cyanide
g. potassium phosphate
h. ammonium sulfate
i. aluminum hydroxide
7. a. $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$
b. $4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$
c. $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$
d. $\text{H}_2\text{SO}_4 + 2\text{NaCN} \rightarrow 2\text{HCN} + \text{Na}_2\text{SO}_4$
e. $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$
f. $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$
g. $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$
h. $\text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2$
8. 56 g CaO
9. 12 g H₂
10. 252 g HNO₃
11. 114 kg C₇H₅N₃O₆
12. 160 g O₂
13. 8 g O₂
14. 2100 g Fe
15. 22 g N₂O
16. 0.5 g H₂
17. 23 g F₂
18. 272 mg H₂O₂
- e. K
f. P
g. O²⁻
h. Na⁺
e. iodine
f. magnesium ion
g. iodide ion
h. chloride ion
- e. FeBr₃
f. Na₂S
g. MgI₂
h. Al₂O₃
f. magnesium nitride
g. iron(II) chloride
h. iron(III) chloride
i. iron(III) oxide
- d. NaNO₃
e. NaHCO₃
f. Ca(OH)₂
- i. Al³⁺
j. Fe²⁺
k. Br⁻
l. N³⁻
i. iron(III) ion
j. sulfide ion
k. calcium ion
l. potassium ion
- g. MgCO₃
h. Na₂SO₄
i. Na₃PO₄

Chapter 7

- H_3O^+ (the hydronium ion)
- OH^- (the hydroxide ion)
- strong acids: HCl (hydrochloric acid), H_2SO_4 (sulfuric acid), HNO_3 (nitric acid); weak acids: $\text{HC}_2\text{H}_3\text{O}_2$ (acetic acid), H_3BO_3 (boric acid)
- strong bases: NaOH (sodium hydroxide), KOH (potassium hydroxide); weak bases: NH_3 (ammonia), $\text{Mg}(\text{OH})_2$ (magnesium hydroxide)
- $\text{HA} + \text{B} \rightarrow \text{HB} + \text{A}$
acid base
- a. acidic b. neutral c. acidic d. basic
- proton donor in each case: HCl ; proton acceptors are CO_3^{2-} , CO_3^{2-} , O^{2-} , OH^- , and HCO_3^- , respectively

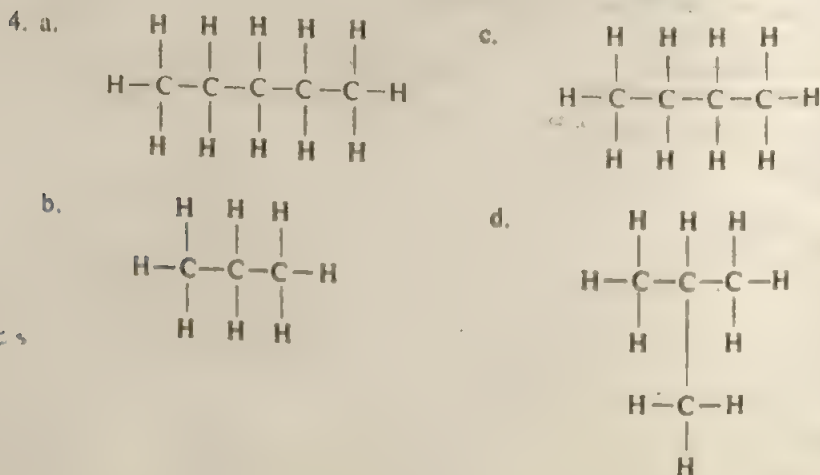
Chapter 8

- a. CO_2 c. NO e. $\text{CO}_2 + \text{SO}_2$
b. SO_2 d. $\text{CO}_2 + \text{H}_2\text{O}$ f. $\text{CO}_2 + \text{H}_2\text{O}$
- I^- is oxidized; Cl_2 is reduced
- MoO_3 is reduced; H_2 is the reducing agent
- O_2 , H_2O_2 , Cl_2 , NaOCl
- H_2 , C, hydroquinone
- H_2CO is oxidized; H_2O_2 is the oxidizing agent
- ethylene is reduced; it gains hydrogen
- 10 800 L of air; 2268 L of O_2
- 160 L of O_2

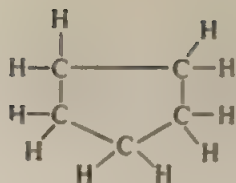
Chapter 9

- constant: N_2 , O_2 , Ar; variable: CO_2 , H_2O
- reduction
- oxidation
- most abundant element: O; second most abundant: Si
- most abundant metal: Al; most widely used: Fe

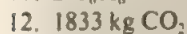
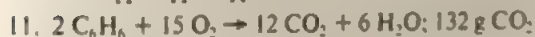
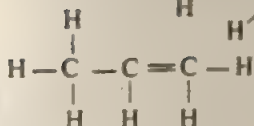
Chapter 10



5.

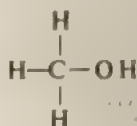


7.

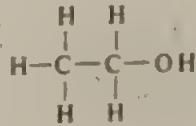


Chapter 11

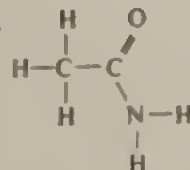
1. a.



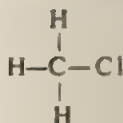
d.



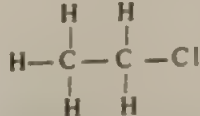
g.



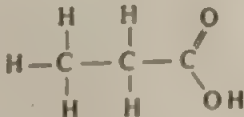
b.



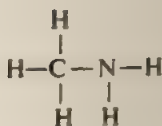
e.



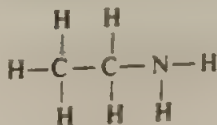
h.



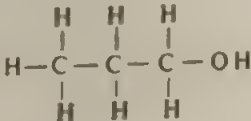
c.



f.



i.



3. a. hydroxyl group (alcohol)

b. amino group

c. acid

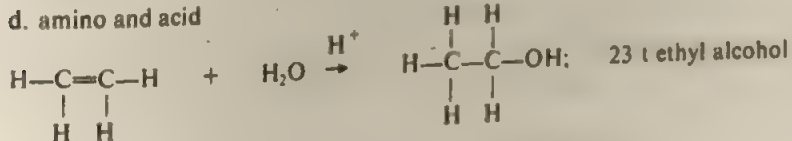
d. amino and acid

e. hydroxyl and acid

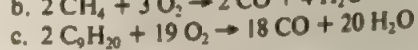
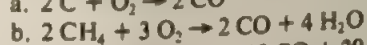
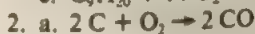
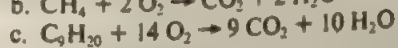
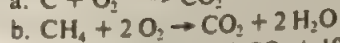
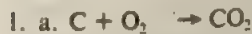
f. amide

g. ketone

10.

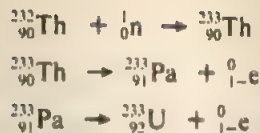
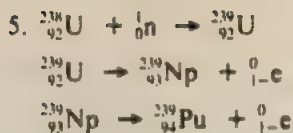


Chapter 12



Chapter 13

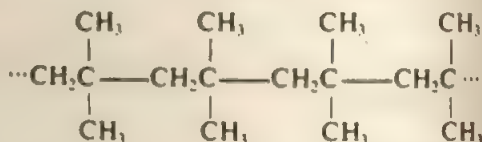
4. by converting nonfissile uranium-238 to fissile plutonium-239



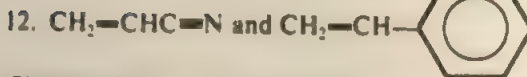
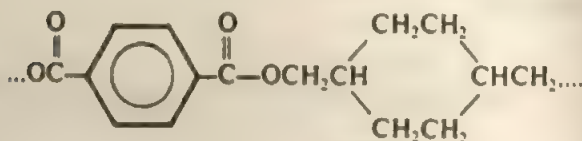
Chapter 14

4. a double bond

10.



11.



Chapter 15

1. 20 years
5. 30 g DDT
6. 300 mg parathion; 0.6 mg soman
8. N, P, K
9. Cu, Mg, S
10. Cu, Fe, Mn, Mo, Zn, Cl, B (any three)

Chapter 16

1. carbohydrates, fats, proteins
9. 4 hours
10. 0.1 hour, or 6 minutes
11. 40 days
15. 258 mi
16. 20%
17. 32.4 g

Chapter 17

1. intentional, incidental
4. a. prevent goiter
b. flavor
c. enhance flavor
d. inhibit bacteria
e. inhibit mold
f. bleach; inhibit bacteria
g. act as antioxidant
h. color
i. sweeten
11. a. butylated hydroxytoluene
b. diethylstilbestrol
c. Food and Drug Administration
d. generally recognized as safe
e. monosodium glutamate
f. polybrominated biphenyls

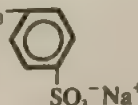
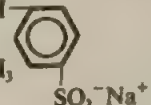
Chapter 18

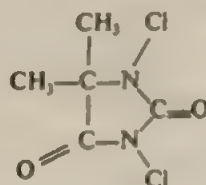
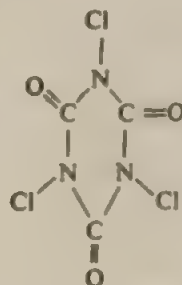
7. Na^+ ; K^+ ; Ca^{2+} ; Mg^{2+} ; sometimes Fe^{2+} or Fe^{3+} ; SO_4^{2-} ; HCO_3^- ; Cl^-
8. O_2 , N_2 , CO_2 , HNO_3 , dust
9. contains Ca^{2+} , Mg^{2+} , sometimes Fe^{2+}
19. 4 million t CaO

Chapter 19

1. N_2 , O_2 , Ar, CO_2 , H_2O , traces of other chemicals
2. carbon monoxide, hydrocarbons, sulfur oxides, particulate matter, nitrogen oxides
4. about \$73 per person; \$292 per family of four
21. a. $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$ d. $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$
 b. $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$ e. $\text{NO}_2 + \text{sunlight} \rightarrow \text{NO} + \text{O}$,
 c. $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ then $\text{O}_2 + \text{O} \rightarrow \text{O}_3$
22. 8000 μg , or 8 mg

Chapter 20

1. a. $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-\text{Na}^+$ g. $\text{Na}_3\text{P}_3\text{O}_{10}$
 b. $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-(\text{HOCH}_2\text{CH}_2)_3\text{NH}^+$ h. NaOCl
 c. $\text{CH}_3\text{CH}(\text{CH}_2\text{CH})_3$  i.
 d. $\text{CH}_3(\text{CH}_2)_8\text{CH}$ 
 e. $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_8\text{H}$ j.
 f. $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{N}^+(\text{CH}_3)_3 \text{Cl}^-$



4. The essential ingredients are usually the following (nonessential ingredients vary):
 a. surfactant (e.g., LAS) f. NaOH (or KOH)
 b. surfactant, solvent g. HCl (or H_3PO_4)
 c. surfactant, abrasive h. CH_3CCl_3 (or H_2SO_4)
 d. surfactant i. NaOH
 e. builders, surfactant j. solvent

Chapter 21

3. an oxidation reaction
5. reductions (breaking $\text{S}-\text{S}$ bonds) and oxidations (forming new $\text{S}-\text{S}$ bonds)

11. A deodorant masks body odors with perfume; an antiperspirant retards perspiration.

Chapter 22

1. in amount or purity of the aspirin present; in 5-grain tablets, there is no significant difference between brands
13. a male sex hormone
14. a female sex hormone
18. antimetabolites, alkylating agents

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58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	67	Ho	68	Er	69	Tm	70	Yb	71	Lu
140.1	140.9	144.2	(147)	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0	175.0														
90	Th	91	Pa	92	U	93	Np	94	Pu	95	Am	96	Cm	97	Bk	98	Cf	99	Es	100	Fm	101	Md	102	No	103	Lr
232.0	(231)	238.0	(237)	(242)	(243)	(247)	(247)	(249)	(254)	(255)	(256)	(257)	(258)	(259)	(260)	(261)	(262)	(263)	(264)	(265)	(266)	(267)	(268)	(269)	(270)	(271)	

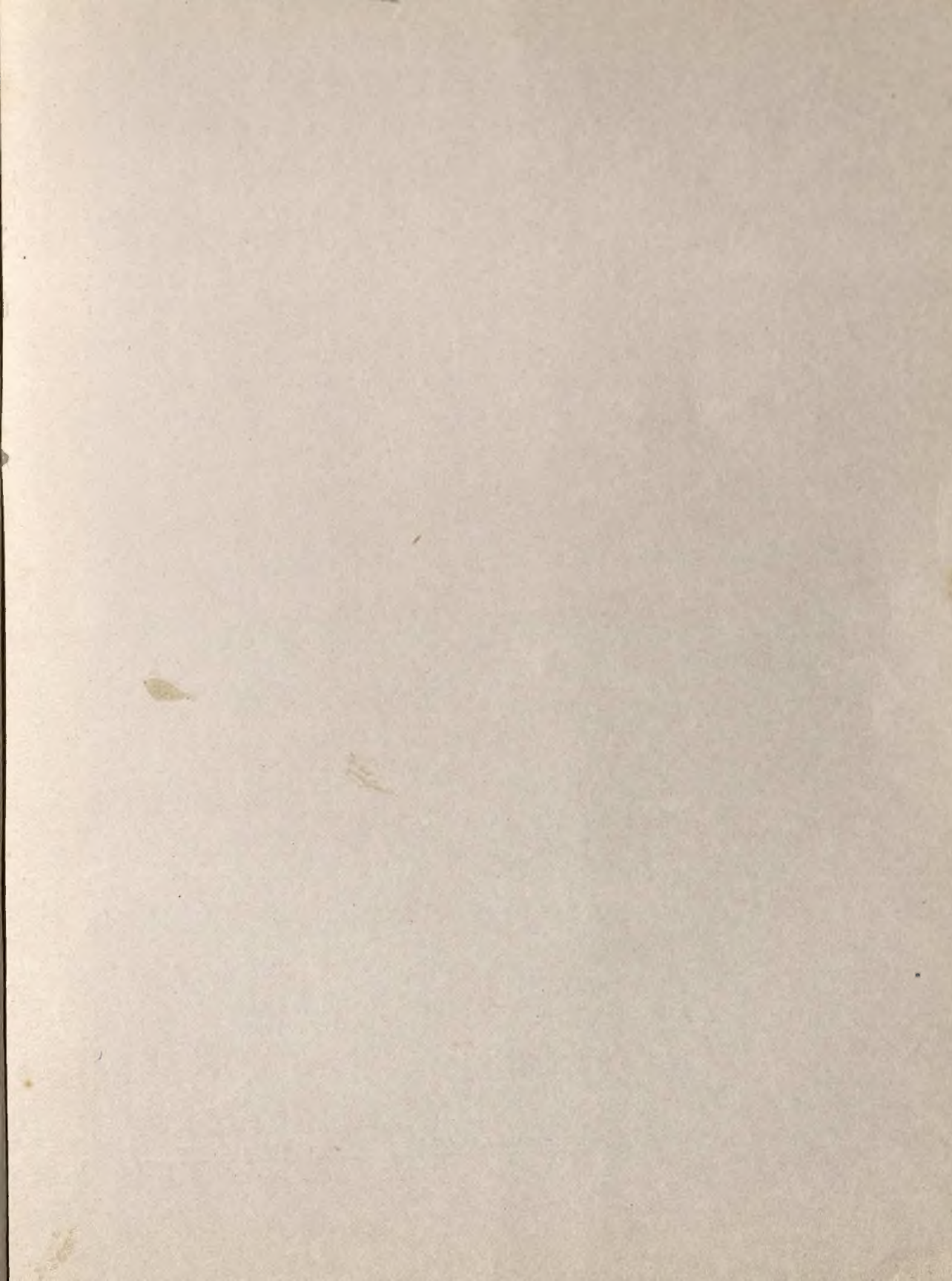
‡ Parentheses around atomic mass indicate that mass given is that of the most stable known isotope.

⁶ Both Russian and American scientists have claimed the discovery of elements 104 and 105. Official names have not been adopted yet.

Table of Atomic Masses (Based on Carbon-12)

Element	Symbol	Atomic Number	Atomic Mass	Element	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	(227)*	Mercury	Hg	80	200.6
Aluminum	Al	13	27.0	Molybdenum	Mo	42	95.9
Americium	Am	95	(243)	Neodymium	Nd	60	144.2
Antimony	Sb	51	121.8	Neon	Ne	10	20.2
Argon	Ar	18	39.9	Neptunium	Np	93	237.0
Arsenic	As	33	74.9	Nickel	Ni	28	58.7
Astatine	At	85	(210)	Niobium	Nb	41	92.9
Barium	Ba	56	137.3	Nitrogen	N	7	14.0
Berkelium	Bk	97	(245)	Nobelium	No	102	(254)
Beryllium	Be	4	9.01	Osmium	Os	76	190.2
Bismuth	Bi	83	209.0	Oxygen	O	8	16.0
Boron	B	5	10.8	Palladium	Pd	46	106.4
Bromine	Br	35	79.9	Phosphorus	P	15	31.0
Cadmium	Cd	48	112.4	Platinum	Pt	78	195.1
Calcium	Ca	20	40.1	Plutonium	Pu	94	(242)
Californium	Cf	98	(251)	Polonium	Po	84	(210)
Carbon	C	6	12.0	Potassium	K	19	39.1
Cerium	Ce	58	140.1	Praseodymium	Pr	59	140.9
Cesium	Cs	55	132.9	Promethium	Pm	61	(145)
Chlorine	Cl	17	35.5	Protactinium	Pa	91	231.0
Chromium	Cr	24	52.0	Radium	Ra	88	226.0
Cobalt	Co	27	58.9	Radon	Rn	86	(222)
Copper	Cu	29	63.5	Rhenium	Re	75	186.2
Curium	Cm	96	(245)	Rhodium	Rh	45	102.9
Dysprosium	Dy	66	162.5	Rubidium	Rb	37	85.5
Einsteinium	Es	99	(254)	Ruthenium	Ru	44	101.1
Erbium	Er	68	167.3	Samarium	Sm	62	150.4
Europium	Eu	63	152.0	Scandium	Sc	21	45.0
Fermium	Fm	100	(254)	Selenium	Se	34	79.0
Fluorine	F	9	19.0	Silicon	Si	14	28.1
Francium	Fr	87	(223)	Silver	Ag	47	107.9
Gadolinium	Gd	64	157.3	Sodium	Na	11	23.0
Gallium	Ga	31	69.7	Strontium	Sr	38	87.6
Germanium	Ge	32	72.6	Sulfur	S	16	32.1
Gold	Au	79	197.0	Tantalum	Ta	73	180.9
Hafnium	Hf	72	178.5	Technetium	Tc	43	98.9
Helium	He	2	4.00	Tellurium	Te	52	127.6
Holmium	Ho	67	164.9	Terbium	Tb	65	158.9
Hydrogen	H	1	1.008	Thallium	Tl	81	204.4
Indium	In	49	114.8	Thorium	Th	90	232.0
Iodine	I	53	126.9	Thulium	Tm	69	168.9
Iridium	Ir	77	192.2	Tin	Sn	50	118.7
Iron	Fe	26	55.8	Titanium	Ti	22	47.9
Krypton	Kr	36	83.8	Tungsten	W	74	183.8
Lanthanum	La	57	138.9	Uranium	U	92	238.0
Lawrencium	Lr	103	(257)	Vanadium	V	23	50.9
Lead	Pb	82	207.2	Xenon	Xe	54	131.3
Lithium	Li	3	6.94	Ytterbium	Yb	70	173.0
Lutetium	Lu	71	175.0	Yttrium	Y	39	88.9
Magnesium	Mg	12	24.3	Zinc	Zn	30	65.4
Manganese	Mn	25	54.9	Zirconium	Zr	40	91.2
Mendelevium	Md	101	(256)				

*Parentheses around atomic mass indicate that mass given is that of the most stable known isotope.





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